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OF

APPLIED CHEMISTRY

VOL. II.

A DICTIONARY OF APPLIED CHEMISTRY

BY

SIR EDWARD THORPE, C.B., LL.D., F.R.S.

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SIR EDWARD THORPE, C.B., LL.D., F.R.S.

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ABBREVIATIONS

OF THE TITLES OF JOURNALS AND BOOKS.

Amer. Chem. J.	American Chemical Journal.
Amer. J. Pharm.	American Journal of Pharmacy.
Amer. J. Sci.	American Journal of Science.
Analyst	The Analyst.
Annalen	Annalen der Chemie (Justus Liebig).
Ann Chim. anal.	Annales de Chimie analytique appliquée à l'Industrie, à l'Agriculture, à la Pharmacie et à la Biologie.
Ann. Chim. Phys.	Annales de Chimie et de Physique.
Ann. Falsif.	Annales des Falsifications.
Ann. Inst. Pasteur.	Annales de l'Institut Pasteur.
Arch. Pharm.	Archiv der Pharmazie.
Bentl. a. Trim.	Bentley and Trimen. Medicinal Plants.
Ber.	Berichte der Deutschen chemischen Gesellschaft.
Ber. Deut. pharm. Ges.	Berichte der Deutschen pharmazeutischen Gesellschaft.
Bied. Zentr.	Biedermann's Zentralblatt für Agrikulturchemie und rationellen Landwirtschafts-Betrieb.
Bio-Chem. J.	The Bio-Chemical Journal.
Biochem. Zeitsch.	Biochemische Zeitschrift.
Brewers J.	Brewers Journal.
Bull. Imp. Inst.	Bulletin of the Imperial Institute.
Bull. Soc. chim.	Bulletin de la Société chimique de France.
Chem. Ind.	Chemische Industrie.
Chem. News	Chemical News.
Chem. Soc. Proc.	Journal of the Chemical Society of London. Proceedings.
Chem. Soc. Trans.	Journal of the Chemical Society of London. Transactions.
Chem. Zeit.	Chemiker Zeitung.
Chem. Zentr.	Chemisches Zentralblatt.
Compt. rend.	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences.
Dingl. poly. J.	Dingler's polytechnisches Journal.
Färber-Zeit.	Färber-Zeitung.
Flück. a. Hanb.	Flückiger and Hanbury. Pharmacographia.
Frdl.	Friedländer's Fortschritte der Teerfarbenfabrikation.
Gazz. chim. ital.	Gazzetta chimica italiana.
Jahrb. Min.	Neues Jahrbuch für Mineralogie, Geologie und Palaeontologie.
J. Amer. Chem. Soc.	Journal of the American Chemical Society.
J. Ind. Eng. Chem.	Journal of Industrial and Engineering Chemistry.
J. Inst. Brewing	Journal of the Institute of Brewing.
J. Pharm. Chim.	Journal de Pharmacie et de Chimie.
J. Phys. Chem.	Journal of Physical Chemistry.
J. pr. Chem.	Journal für praktische Chemie.
J. Russ. Phys. Chem. Soc.	Journal of the Physical and Chemical Society of Russia.
J. Soc. Chem. Ind.	Journal of the Society of Chemical Industry.
J. Soc. Dyers.	Journal of the Society of Dyers and Colourists.
Min. Mag.	Mineralogical Magazine and Journal of the Mineralogical Society.
Monatsh.	Monatshefte für Chemie und verwandte Theile anderer Wissenschaften.
Pharm. J.	Pharmaceutical Journal.
Pharm. Zeit.	Pharmazeutische Zeitung.
Phil. Mag.	Philosophical Magazine (The London, Edinburgh and Dublin).
Phil. Trans.	Philosophical Transactions of the Royal Society.
Phot. J.	Photographic Journal.
Proc. Roy. Soc.	Proceedings of the Royal Society.
Rec. trav. chim.	Receuil des travaux chimiques des Pays-Bas et de la Belgique.
Zeitsch. anal. Chem.	Zeitschrift für analytische Chemie.
Zeitsch. angew. Chem.	Zeitschrift für angewandte Chemie.
Zeitsch. anorg. Chem.	Zeitschrift für anorganische Chemie.
Zeitsch. Nahr. Genussm.	Zeitschrift für Untersuchung der Nahrungs- und Genussmittel.
Zeitsch. öffentl. Chem.	Zeitschrift für öffentliche Chemie.
Zeitsch. physikal. Chem.	Zeitschrift für physikalische Chemie, Stöchiometrie und Verwandtschaftslehre.
Zeitsch. physiol. Chem.	Hoppe-Seyler's Zeitschrift für physiologische Chemie

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CHIAN TURPENTINE *v.* OLEO-RESINS.

CHICA RED. *Chica red* or *chica, carneru, Vermillon americanum, carajura* is a red pigment, produced by the Indians of Central America from *Bignonia chica* (Humb. et Bonpl.). The leaves of this plant are extracted with boiling water, and the extract is allowed to ferment, or, according to Crookes (Dyeing and Calico-printing), some particles of the bark of a tree called 'aryane' are added to the liquid, and cause the precipitation of the colouring matter.

Chica red came into commerce in the form of small red cakes under the name of 'carneru,' or 'vermillon americanum,' and sometimes as a red powder; but is now extremely difficult, if not impossible, to procure. It is insoluble in water, somewhat soluble in boiling dilute alcohol, and soluble in solutions of the alkali hydroxides, with a brown-red or orange-red colour.

Boussingault (Ann. Chim. Phys. [2] 27, 315) extracted from this material, by means of alcohol, a red colouring matter. Erdmann (J. 1857, 487) employed alcoholic sulphuric acid, and precipitated the dye with ammonium carbonate. According to the latter author, this product has the composition $C_8H_8O_4$, and is decomposed by nitric acid with formation of anisic acid, picric acid, oxalic acid, and hydrocyanic acid.

Chica red is in reality a lake, and when this is decomposed with hot dilute hydrochloric acid, a comparatively small quantity of a residue remains, which consists of a mixture of the free colouring matter with plant *debris*. After purification the colouring matter consists of a pale-red power, soluble in alkaline solutions, with a red-violet colouration, which rapidly becomes brown on contact with air. It dyes mordanted calico shades which are of a similar type to those given by alizarin. *Carajura*, which is also a lake, appears to yield the same dyestuff as chica red, and is probably identical with it (Perkin, private communication). A. G. P.

CHICAGO BLUE, -ORANGE, *v.* AZO- COLOURING MATTERS.

CHICK PEA. *Cicer arietinum*, L. A leguminous annual, growing to a height of about 2 feet, largely cultivated in India, where its seeds are used as food for cattle and horses, and, after the removal of the husks, for man.

In some cases the young leaves, fried in oil, are also eaten. Church (The Food Grains of India, 1886) gives, as the average composition:

	Water	Protein	Fat	Sol. carbohydrates	Fibre	Ash
With husk	11·2	19·5	4·6	53·8	7·8	3·1
Husked	11·5	21·7	4·2	59·0	1·0	2·6

Analyses of various parts of the fresh plant were made by Passerini (Staz. Sper. Agrar. 21, 20; Chem. Soc. Abstr. 1893, ii. 226).

The fresh substance of the stems, leaves, and entire pods contained 27·54 p.c., 24·39 p.c., and 19·85 p.c. of dry matter respectively.

The dry matter of the stems, leaves, and seeds contained:

	Protein	Fat	Cellulose	Other carbohydrates	Ash	Nitrogen
Stems	6·35	1·8	35·0	49·0	7·81	1·62
Leaves	14·21	4·1	13·9	58·9	8·83	2·27
Seeds	26·20	5·2	1·7	63·6	3·30	4·19

The ash contained:

	K_2O	Na_2O	CaO	MgO	Fe_2O_3	Mn_3O_4	P_2O_5	SO_3	SiO_2	Cl
Stems	48·4	0·5	23·6	4·4	2·1	0·03	5·3	5·8	6·2	3·7
Leaves	29·6	0·9	40·6	3·3	3·0	—	6·0	4·4	11·3	1·8
Seeds	24·6	1·3	4·5	20·0	2·4	—	39·6	3·4	0·7	2·9

Traces of boron, lithium, and copper were also present in the ash. H. I.

CHICORY or SUCCORY. *Cichorium Intybus* (Linn.). A perennial plant belonging to the *Compositæ*, growing to a height of about 3 feet, bearing blue flowers and having a long tap root. It is sometimes grown as cattle food, the foliage being thus used, but more generally it is cultivated for the sake of its root, which, when dried, roasted, and ground, is largely used for mixing with coffee.

According to Letheby's analysis (quoted by Wynter Blyth, Foods, 359, 1909), fresh chicory root contains:

Water	Gummy matter	Glucose	Bitter extractive	Fat	Cellulose, inulin, and fibre	Ash
77·0	7·5	1·1	4·0	0·6	9·0	0·8

Analyses by Mayer (Bied. Zentr. 1885, 828) gave:

Water	Albuminoids	Fat	Inulin	Fibre	Sugar	Bitter extract	Ash
72 to 77	1·1	0·2	12·0 to 17.3	1·4 to 1·8	5·6 to 6·0	0·5 to 0·15	1·4 to 1·9

Wolff (Chem. Zentr. 1899, ii. 211) also found that chicory root contains from 13 to 15 p.c. of inulin, and an optically inactive sugar, synanthrose. He states that drying the roots has little or no effect upon the sugars, but during roasting the reducing sugars are increased, a large portion of the inulin is changed, and caramel and dextrin are formed.

Petermann (Bied. Zentr. 1883, 843) found pure roasted chicory to contain:

Soluble in water, 74·2 p.c.

Water	Glucose	Dextrin and inulin	Protein	Colouring matter	Ash
16·3	26·1	9·6	3·2	16·4	2·6

Insoluble in water, 25·8 p.c.

Protein	Fat	Cellulose	Ash
3·2	5·7	12·3	4·6

The ash of chicory root and leaves, according to Wolff, contain:

	K_2O	Na_2O	MgO	CaO	Fe_2O_3	P_2O_5	SO_3	SiO_2	Cl
Root	40·4	7·7	6·3	8·7	3·0	14·2	9·0	6·0	3·7
Leaves	60·0	0·7	3·2	14·3	—	9·0	9·0	1·0	1·7

Wynter Blyth (Foods, 359, 1909) gives as the main differences between the ashes of coffee and chicory, the following:—

	Coffee ash	Chicory ash
Silica and sand	—	10·7–35·9 p.c.
Carbon dioxide	14·9	1·8–3·2 „
Ferric oxide	0·44–0·98	3·1–5·3 „
Chlorine	0·26–1·1	3·3–4·9 „
Phosphorus pentoxide	10·0–11·0	5·0–6·0 „

The soluble ash of chicory may be taken as about 1·74 p.c., that of coffee as about 3·0 p.c.

Chicory has about three times the tinctorial power of ordinary coffee, and this has been proposed as the basis for a rough estimation of the amount of chicory present in a mixture of coffee and chicory (Leebody, Chem. News, 30, 243).

The sp.gr. at 15·5° of a solution, made by boiling a quantity of the substance with ten times its weight of water, affords a ready method of approximately determining the amount of adulteration. The following table gives the specific gravities of infusions made in this way from the various substances:—

Spent tan	1·00214
Acorns	1·00730
Peas	1·00730
Mocha coffee	1·00800
Ceylon coffee	1·00870
Java coffee	1·00870
Costa Rica coffee	1·00900
Native Ceylon coffee	1·00900
Brown malt	1·01090
Black malt	1·02120
Dandelion root	1·02190
Red beet	1·02210
Yorkshire chicory	1·01910
Foreign chicory	1·02260
Guernsey chicory	1·02326
Maize	1·02530
Bread raspings	1·02630

(quoted by Wynter Blyth, Foods, 360).

Hehner and Skertchly propose a determination of furfural (a measure of pentosans) as a means of examining suspected coffee. Coffee gives about 5–5·5 p.c., chicory about 2·5 p.c. of pentosans (Analyst, 24, 178). H. I.

CHILE SALTPETRE. *Sodium nitrate* (*v.* SODIUM).

CHINA BLUE. Syn. *Water Blue, Cotton Blue, Opal Blue v.* TRIPHENYLMETHANE COLOURING MATTERS.

CHINA CLAY or KAOLIN *v.* CLAY.

CHINA GRASS. *Rhea Ramie fibre.* This substance is the fibre of two (or perhaps more) species or varieties of the genus *Boehmeria*, nat. ord. *Urticaceæ*, shrubs allied to the nettle (*Urtica*), but possessing no stings, namely, *Boehmeria nivea* (Hook and Arn.) with a white hairy under surface to the leaf, and *B. utilis* [*B. tenacissima* (Gaud.)] with a green (Blume) under surface (more or less hairy only on the nerns) to the leaf. It is the Tchou-ma of China and the Rheea of Assam. The plants grow to a height of from three to five feet, throwing up numerous straight shoots as thick as the little finger, and covered with short soft hairs. Its leaves grow upon long foot-stalks and are broadly heart-shaped, about six inches long by four broad. It is a native of China and Sumatra, where, as in India, it has long been cultivated.

Its manufacture into mats used for making sails, foot-mats, &c., is carried on in Southern China, where three crops of Tchou-ma are taken each year, of which the second is the best. For this purpose the grass is sorted into bundles, which are soaked in water for two or three days and then dried in the sun. If a red colour is desired, the grass is steeped in a decoction of sapan wood; if yellow, in a decoction of the seeds and flowers of the common Chinese plant *mi-fa*, or in one of *Sophora japonica*, to which a little alum is added as a mordant. Other vegetable dyes are also employed; but of late years aniline colours have in a measure taken their place.

By processes of manufacture an exceedingly fine fibre is produced on separating the filaments of the stalk—a fibre distinguished by its strength, which is nearly three times that of Russian hemp; by its length, which is greater than that of any bast product; and by its lustrous, silky appearance. Great efforts have been made, with more or less success, to render the use of the fibre in European textile manufactures commercially profitable. It will be seen from the following remarks that there are difficulties in the way. In the first place, the method of separating the bast by hand was tedious, and could only be performed whilst the stems were quite fresh, thus limiting its production to the immediate neighbourhood of the plant's growth. In China the bark is stripped from the stems and the fibre scraped off with a knife, a process which removes the whole so-called grass if performed while the stem is still quite fresh, but leaves a large portion if it has become at all dry. Even under the best conditions a very skilful operator can collect only two pounds of grass per day, the average quantity obtained being only half a pound to one pound. It is further found that, owing to the large amount of pectinic substances

contained in these *Urticaceæ*, the long steeping or retting processes used with flax and hemp cannot be practised on account of the ensuing excessive fermentation, which injures the fibre. Experiments made in India with unskilled workers gave about four ounces per day each as the result of their labour. Attention has consequently been given to mechanical processes for separating the fibres from the bark in the green and in the dry state. With this in view, the India Office some years ago submitted samples of the dried article to Dr. Forbes Watson, who reported that he did not find it at all difficult to obtain the fibre from stems which were quite dry. The difficulty in the case of India is that the best crops are obtained during the rainy season, when it is all but impossible to dry the stems except by expensive artificial means; while, as above pointed out, the liability of the plant to ferment resulted in the spoiling of the crops when its treatment was delayed. The Government of India has followed up its inquiries and encouraged inventors to competition in producing a machine capable of dealing with the green crop. It may be said that this encouragement has resulted in an approximation to success; thus, in one instance of a machine consisting of a cylinder with beaters revolving at a high speed against the stems upon which meanwhile a jet of water is poured, Dr. Watson estimated the cost of producing the fibre to average 4*l.* to 5*l.* per ton. The yield from the machine was from 1 to 2 tons of green stalks per day, estimated to produce about 100 lbs. of cleaned fibre.

In the treatment of green stalks by hand the Favier's process consists in subjecting the plants to the action of steam for 15 to 30 minutes, after which the bark is easily stripped. Those stems also which have been standing some time after being cut can also be treated without leaving any appreciable amount of fibre on the stalks.

The operation of scutching the dried stems presents no difficulty when steam power is applicable and when the quantity of material to be treated is sufficiently large. The next process, however, of 'ungumming' has given a little trouble. Since China grass contains from 22 to 28 or, in some cases, up to 35 p.c. of gum, it is necessary to remove this constituent of the fibre before it can be spun into yarn. For this purpose many partly mechanical and partly chemical processes have been devised. It may sufficiently describe the lines which these various systems take to say that they resemble generally the processes adopted in the scouring and bleaching of cotton goods—that is to say, by subjecting the material to pressure under the application of steam, and to alternate treatment of alkaline and acid agents.

China grass has little or no attraction for dyes, and consequently the methods adopted in the dyeing of cotton or of jute are applicable to it. It is found that mineral colours, such as chrome yellow and orange, destroy the peculiar lustre of China grass; the yellow dye obtained with cadmium sulphide, however, is not open to this objection. Alizarin mordanted with Turkey-red oil destroys the lustre, whilst aniline colours fixed with the same mordant do not. Rosaniline derivatives and azo- colouring matters may be used satisfactorily. It is recommended that the grass should be dyed immediately after retting and before spinning, to preserve the characteristic sheen.

The textiles formerly associated with China grass were such articles as handkerchiefs and 'grass cloths,' imported direct from China; but recent efforts to introduce the manufacture as well as the growth of China grass into Europe have led to other developments. Thus at the manufactory of Zittau in Saxony, the fibre has found application in tapestry and dress goods, table-cloths, damasks, lace, fancy knitting yarns, &c. It is also used in the manufacture of incandescent gas-mantles.

A number of other species of *Boehmeria* also supply bast fibres.

CHINA INK *v.* INDIAN INK.

CHINA-STONE. A granitic rock, having its felspathic constituent more or less decomposed, but not completely kaolinised. As the felspar still retains part of its alkali, and as some micaceous mineral is generally present, the stone is fusible; hence it is largely used in the manufacture of porcelain, and when free felspar is not introduced it forms the only vitrifiable constituent of the paste. China-stone is sometimes known as 'Cornish stone' in consequence of its being largely quarried in Cornwall, where it was discovered by W. Cookworthy, of Plymouth, about 1750. He first noticed it at Tregonning Hill, near Breage, and described it under the local name of 'growan' or 'moor-stone.' It is now obtained principally from the neighbourhood of St. Stephens, near St. Austell. The rock requires no preparation, but is sent direct from the quarry to the potteries. Notwithstanding the altered condition of the felspar, it is used locally as a building stone, and found to be durable.

The conditions under which the china-stone has been formed are obscure. Its occurrence sometimes in narrow bands, and its altered character at great depths, render it improbable that the decomposition has been due to the superficial action of meteoric agents, such as water and carbon dioxide. Daubrée, Smyth, Le Neve Foster, Collins, and other observers in Cornwall, have held that the granite has been decomposed probably by means of compounds containing fluorine rising from below; a view supported by the fact that the china-stone and kaolin occur in association with veins of tin ore and various fluorine-bearing minerals (Daubrée, Geol. Expt. 1879, 64).

Cornish stone consists usually of quartz, altered orthoclase, kaolinite, and gilbertite, frequently associated with lepidolite, or lithia-mica, known to the Cornish quarrymen as 'shell,' and occasionally as schorl, or black tourmaline, and fluor-spar as accessory constituents. The gilbertite (hydrated silicate of aluminium and potassium) seems to have been mistaken by some observers for talc (hydrated silicate of magnesium), as the china-stone has been frequently described as an altered talcose granite. The following analyses of the china-stone of St. Stephens, Cornwall, are given by J. H. Collins (Hensbarrow Granite District, Truro, 1878, 31):—

Silica	73·39	69·50	71·66
Alumina	16·50	17·85	18·79
Lime	0·50	2·66	1·70
Magnesia	0·31	0·12	0·35
Potash (with a little soda)	7·66	7·98	6·60
Iron	trace	trace	trace
Manganese	—	trace	trace
Fluorine	0·74	0·71	0·14
Water	1·25	1·30	0·91
	100·35	100·12	100·15

It has been proposed by Collins to distinguish china-stone under the name *petunzite*, a word suggested by the Chinese *pe-tun-tse*. In the early part of the 18th century a Jesuit missionary named D'Entrecolles, residing at King-te-chin, sent to Réaumur, in Paris, samples of the raw materials used in China. These were the first specimens of their kind that had ever reached Europe, and they led to the foundation of the manufacture of procelain at Sèvres. The china-stone was described by D'Entrecolles as pe-tun-tse, and the china-clay as kaolin; but it appears that the former name, if not both, must have been erroneously applied. According to the Chinese scholar, Stanislas Julien (Hist. et Fabric. de la Porcel. Chin. Paris, 1856, preface xx.), *pe-tun* signifies 'white paste,' while *tse* is merely a diminutive applied to the material when worked up into small cakes. Hence, pe-tun-se is really the name of small blocks of white clay or prepared paste, and not of the granitic rock. Nevertheless, custom in this country has justified the use of the term *pe-tun-tse* as synonymous with china-stone.

(For an account of the occurrence of china-stone in Cornwall, *see* Mem. Geol. Survey, Bodmin and St. Austell District, 1909.) The amount of china-stone raised in Cornwall in 1908, and sent as such to the potteries, was 75,473 tons, valued at 37,315*l.*; while the amount of china-clay washed from china-stone at the pits amounted during the same period in Cornwall and Devon to 721,416 tons, valued at 484,305*l.* F. W. R.

CHINESE BLUE. (*Porzellanblau*, Ger.) Several compounds are sold under this name, of which the following are examples: ultramarine and flake white; cobalt blue and white lead; and a double cyanide of iron (Prussian blue) (*v.* PIGMENTS).

CHINESE GREEN or LOKAO. This colouring matter is obtained in China from different varieties of buckthorn (*Rhamnus*), and is brought into commerce in the form of thin blue slabs, easily broken, but difficult to pulverise. It is a lake containing the colouring matter lokaïn, with from 26 p.c. (Cloez and Guignet, Ber. 5, 338) to 47 p.c. of clay and chalk (Kayser, *ibid.* 18, 3417). To obtain the pure colouring matter, lokao is extracted with ammonium carbonate solution; on the addition of alcohol to the filtrate a deep-blue precipitate of the ammonia compound of lokaïn $C_{42}H_{48}O_{27}$ is formed. From the solution of this compound in water, oxalic acid precipitates lokaïn, which, when dried, is a pulverulent bluish-black susbtance insoluble in water, alcohol, ether, chloroform, and benzene. Friction imparts to it metallic lustre. The monammonium salt forms small crystals with bronze-like lustre, from which the diammonium salt $C_{42}H_{46}O_{27}(NH_4)_2$ is obtained by moistening them with ammonia and subsequently drying over sulphuric acid. The barium salt $C_{42}H_{46}BaO_{27}$ is insoluble in water and alcohol. The potassium salt $C_{42}H_{46}K_2O_{27}$ forms a dark-blue amorphous precipitate from alcohol. Soluble compounds of lokaïn show perfect absorption of the spectrum in the red and yellow portions only. Boiling dilute acids decompose lokaïn into a carbohydrate lokaose $C_6H_{12}O_6$, and lokanic acid $C_{36}H_{36}O_{21}$; the latter is a bluish-violet crystalline powder insoluble in water, alcohol, and ether, containing 1 molecule of water, which is given off at 120°. The ammonium salt $C_{36}H_{35}O_{21}NH_4$ is a deep-blue powder soluble in water, with a violet colour; the barium and lead salts are dark-blue powders insoluble in water and alcohol. Soluble compounds of lokaïn in very dilute solution show a characteristic perfect absorption in the yellow and yellow-green portions of the spectrum. Lokaose reduces Fehling's solution with half the power of glucose, from which it also differs by its optical inactivity. The decomposition of the lokaïn is expressed by the equation $C_{42}H_{46}O_{27} = C_{36}H_{36}O_{21} + C_6H_{12}O_6$. Reducing agents convert blue solutions of lokaïn and lokanic acids into blood-red solutions, which become green on exposure to the air.

Lokanic acid is decomposed by cold concentrated sulphuric acid according to the equation $C_{36}H_{36}O_{21} - 5H_2O = C_{36}H_{26}O_{16}$. This latter substance forms a red-brown powder; its barium compound $C_{36}H_{24}BaO_{16}$ is also a red-brown substance. Concentrated potassium hydroxide solution (50 p.c.) decomposes lokanic acid into a brown powder and phloroglucinol; the former body is termed delokanic acid $C_{15}H_9O_6$ (R. Kayser, *l.c.*; J. Soc. Chem. Ind. 5, 162) (*v.* LOKAW).

CHINESE LAKE or SCARLET LAKE *v.* PIGMENTS.

CHINESE VEGETABLE TALLOW is the hard fat which coats the seeds of the Chinese tallow tree, *Stillingia sebifera* (Willd.), *Stillingia sinensis*, *Croton sebiferum*, *Sapium sebiferum*, (Roxb.), *Excœcaria sebifera* (F. Müll), *Carumbium sebiferum*), a tree growing wild in China, and largely cultivated there, as also in Indo-China and the North of India, where the tree thrives luxuriantly. In China the stillingia tree is exploited for both its leaves and seeds. In Tonkin the tree is only cultivated for the sake of its leaves, a decoction of which furnishes a colouring matter used for dyeing silk. In China the fat is only a by-product. The tree commences to produce at the age of 4–5 years, and when it has reached its full development it yields about 24–30 kilos. of seeds a year. The fruit yields about 30 p.c. of a mixture of vegetable tallow and of stillingia oil; half of this quantity consists of vegetable tallow alone, and the other half of stillingia oil. The fruit consists of three oval seeds surrounded by a thick tallow-like mass, the true vegetable tallow. This is recovered by placing the seeds in perforated cylinders and steaming them, so that the fat melts and runs off. Another method is to pass the seeds between fluted rollers, which scrape off the outer fat coating without breaking the seed proper. The scraped-off mass is pressed in the hot in primitive wedge presses, and sold under

the Chinese name of 'pi-iéou' or 'pi-yu'; it is known in Europe as 'prima' vegetable tallow. The seeds which have been bared from their fat coating, are then crushed separately and yield the stillingia oil, a drying oil known in China as 'tsé-tiéou' or 'ting-yu.' In another process, the seeds, together with their coating of fat, are crushed, and thus a mixture of vegetable tallow and stillingia oil is obtained. The product thus prepared is naturally much softer than the true vegetable tallow, and has therefore a lower melting-point and a much higher iodine value. This second quality is sold in Europe as 'secunda' vegetable tallow, and represents a mixture of 'pi-yu' and 'ting-yu.' It is sold in China under the name 'mou-iéou.'

The saponification value of commercial samples of vegetable fat varies, therefore, according to the mode of preparation, from 179 to 203. Similarly, the iodine value varies considerably, and numbers ranging from 19 to 32 have been recorded. The composition of vegetable tallow has not yet been definitely ascertained. From the absence of stearic acid, it may be concluded that the fat consists of palmitin and olein only.

Vegetable tallow plays, in China, an important *rôle* as an article of commerce; it is largely used in the manufacture of candles. During recent years considerable quantities have been exported; thus during 1907 the United Kingdom imported 4000 tons, France 2500 tons, and Italy 1700 tons. The bulk of the vegetable tallow is used in the candle and soap industries. J. L.

CHINESE WAX or **INSECT WAX** *v.* WAXES.

CHINESE YELLOW (*King's yellow*) *v.* PIGMENTS.

CHINOFORM. Trade name for quinine formate.

CHINOLINE *v.* QUINOLINE.

CHINOSOL. Trade name for *o*-hydroxyquinoline sulphate, a pale-yellow crystalline powder with a saffron-like smell and a burning taste; m.p. 175°–177·5°; readily soluble in water, sparingly soluble in alcohol, insoluble in ether; with ferric chloride gives an intense green colour, and a white precipitate with barium chloride. Used as an antiseptic.

CHINOVOSE *v.* CARBOHYDRATES.

CHIOLITE. A double fluoride of aluminium and sodium $3AlF_3 \cdot 5NaF$, closely akin to cryolite $AlF_3 \cdot 3NaF$. Found at Miask (Brandl, Jahrb. Min. 1882; 2nd Ref. 201; Chem. Soc. Abstr. 44, 29).

The following analysis is given by Brandl (Annalen, 213, 1):—

Al	Na	F
17·66	24·97	57·30 = 99·93
17·64	25·00	57·30 = 99·94

CHITIN, CHITOSE *v.* CARBOHYDRATES.

CHLOANTHITE. Native nickel arsenide, $NiAs_2$, isomorphous with smaltite ($CoAs_2$), there being no sharp line of demarcation between the two species. Found as cubic crystals and compact masses at Schneeberg in Saxony and Riechelsdorf in Hesse, where it was formerly mined as an ore of nickel. L. J. S.

CHLORACETIC ACIDS *v.* HALOGEN ACETIC ACIDS.

CHLORAL *Trichloracetaldehyde* $CCl_3 \cdot CHO$.

Chloral was first prepared by Liebig, who obtained it by the continuous chlorination of absolute alcohol (Annalen, 1, 189). It was further examined by Dumas (Ann. Chim. Phys. [2] 56, 125), who determined its composition, and by Städeler (Annalen, 61, 101). Although a chlorinated aldehyde, it cannot be prepared by treating acetaldehyde with chlorine, unless water is present together with calcium carbonate to neutralise the hydrogen chloride formed, since butyric chloral results when dry materials are employed (Pinner, Ber. 4, 256).

Industrial preparation. The process by which chloral is manufactured is divided into three stages: the preparation of chloral alcoholate; conversion of this into chloral; and the formation of chloral hydrate.

In a large glass balloon 60 kilos. of alcohol, as completely dehydrated as possible, are subjected to the action of a current of chlorine, the escaping hydrochloric acid being absorbed by water. The introduction of the chlorine lasts a considerable time, in some works 10 to 14 days. At first the balloon must be cooled, for, if the temperature is not properly regulated, the yield is much reduced. After a time the reaction becomes less violent; the mixture is then warmed to 60°, and finally to 100°. When the liquid is completely soluble in water, the current of chlorine is stopped, and on cooling, a white mass of the alcoholate is obtained. In this operation Springmühl recommends the use of iodine as a chlorine carrier; Page, the addition of crystallised ferric chloride (Annalen, 1884, 225, 209); and in either case the ethyl halide is easily recovered.

In the ordinary process the chlorinated liquid is not allowed to cool, and is transferred to an enamelled still holding 150–200 kilos., where an equal volume of strong sulphuric acid is added in small quantities. The temperature is raised to boiling, the condensed vapours being returned to the still. During the ebullition there is an evolution of hydrochloric acid gas, the cessation of which indicates the termination of the decomposition of the alcoholate. Fractional distillation follows, this ceasing when the thermometer has reached 100°. The distillate is again rectified, the portion coming over above 94° being pure chloral. In some works the final purification is carried out by distilling over chalk or sodium bicarbonate. Ethylene dichloride, ethylidene chloride, and chlorinated ethylene dichloride (b.p. 115°) are also formed as by-products in this reaction (Krämer, Ber. 3, 257).

The chloral is shaken with the theoretical quantity of water and the product of the reaction at once poured over a smooth surface, when it solidifies; in this state it is sent into commerce. To obtain crystals the warm mass (heat is disengaged in this reaction) is mixed with one-third of its volume of chloroform, and the mixture allowed to cool in closed vessels; crystallisation is complete in a week. The mother liquors serve for a second crystallisation, and the crystals are dried at the ordinary temperature. Flückiger (Zeitsch. Chem. [2] 6, 432) recommends crystallisation from

warm carbon disulphide or turpentine, and Martius from benzene. Other methods, which have been described, differ from the preceding in that the chlorinated mixture, after solidification and pressure, is sublimed or distilled with calcium chloride (Detsényi, Dingl. poly. J. 209, 224; Trillat, J. Pharm. Chim. 5, 218).

The following method has been devised for the continuous production of chloral. Chloral and its hydrate are the most volatile products of the action of chlorine on alcohol, and may therefore be removed by continuous distillation. A special apparatus is described; chlorine and chlorinated alcohol are introduced into a vessel heated in a water-bath, from which the vapours pass into a second and then into a third heated vessel. The residual chlorine is absorbed in a cylinder provided with baffle plates. The rectifier, which also acts continuously, is provided with baffle plates; it is fed at the middle with chloral, and at the top with sulphuric acid (66°B.). The final rectification is carried out as already described. The same apparatus may be used for converting chloral into chloroform (Besson, Eng. Pat. 17202; U.S. Pat. 774151; J. Soc. Chem. Ind. 1901, 1139).

Theories to explain the action of chlorine on alcohol and the subsequent production of chloral have been proposed by Lieben (Ber. 3, 910); Wurtz and Vogt (Compt. rend. 74, 777); Jacobsen (Ber. 15, 601); and Brochet (Bull. Soc. chim. 17, [3] 228).

Chloral is a colourless pungent liquid, which solidifies at −75° (Berthelot, Ann. Chim. Phys. [5], 12, 536), at −57·5° (Van Rossem. Zeitsch. physikal. Chem. 1908, 62, 681); and is readily soluble in water, alcohol, and ether. Its b.p. is 97·7° (corr.) and sp.gr. 1·54175 at 0° (Passavant, Chem. Soc. Trans. 39, 55; Thorpe, *ibid.* 37, 191); b.p. 96°–97° at 750 mm., and sp.gr. 1·5121 at 20°/4° (Brühl, Annalen, 203, 11); b.p. 97° at 740 mm. (Van Rossem, *l.c.*). Three hydrates exist: (1) a semihydrate $2C_2HCl_3O,H_2O$; true m.p. is about 49°, the highest observed 80°; (2) the ordinary monohydrate existing in two pseudo-symmetrical modifications; true m.p. 47·4°, highest observed 54°; (3) a heptahydrate, m.p. −14° (Pope, Chem. Soc. Proc. 1896, 142; and Van Rossem, *l.c.*). According to Wolf (J. Phys. Chem. 4, 21); there is only one modification, the difference in melting-points being due to dissociation. Nascent hydrogen reduces it to aldehyde (Personne, Annalen, 157, 113), which it closely resembles in reducing ammoniacal silver nitrate solution (Städeler, Annalen, 106, 253), and in forming crystalline compounds with sodium disulphite (*ibid.*); with ammonia (*v.* chloral ammonium); with hydrogen cyanide (Bischoff and Pinner, Ber. 5, 113; Annalen, 179, 77); with amides (Wallach, Ber. 5, 251; Sulzberg, D. R. P. 198715; J. Soc. Chem. Ind. 1908, 958); and with amines (Wallach, *l.c.*; Rügheimer, Ber. 1906, 1653; Wheeler, Amer. Chem. J. 1902, 1063; 1908, 136; 1909, 937).

When heated with aqueous alkalis it decomposes into chloroform and an alkaline formate, and a similar reaction occurs when alcoholic potash or soda is employed (Kekulé, Annalen, 119, 188). Chlorine, bromine, or iodine and aluminium chloride convert chloral into hexachlorethane (Mouneyrat, Bull. Soc. chim. 17, [3] 796). Fuming nitric acid converts it into trichloracetic acid, and, according to Grabowski (Ber. 6, 225), fuming sulphuric acid combines with it in the cold, but on heating converts it into chloralide $C_5H_2Cl_6O_3$ (compare Grabowski, Ber. 8, 1433; Städeler, Annalen, 61, 114; Wallach, *ibid.* 193, 1). Chloral condenses with succinic acid by means of acetic anhydride to form trichloromethylparaconic acid (Fittig and Miller, *ibid.* 255, 43).

Derivatives. **Chloral ammonium** $C_2H_4Cl_3NO$ is prepared by the action of ammonia on a solution of chloral in chloroform (Schiff, Ber. 10, 167). It is a white crystalline solid, resembling chloral hydrate in taste and colour; it melts at 64°, and is slightly soluble in water, more readily soluble in alcohol (Personne, Annalen, 157, 113; Compt. rend., 71, 228). Nesbit recommends the use of chloral ammonium instead of urethane and chloral hydrate, since the action of chloral hydrate on the respiration centres and the heart is retarded by the introduction into that compound of an amino- group (J. Soc. Chem. Ind. 1889, 413; 1890, 889). By heating chloral ammonium on the water-bath, chloroform and ammonia distil off, and the residue consists of formamide and *chloralimide* $C_2H_3Cl_3N$, the latter of which is extracted with alcohol. *Iso*chloralimide is also formed, and according to Schiff (Gazz. chim. ital. 21, 490), dimolecular and trimolecular -imides exist. Chloralimide can also be prepared by heating chloral and chloral ammonium until chloroform is no longer evolved, and by the reaction between chloral hydrate and ammonium acetate (Schiff, *l.c.*; Pinner and Fuchs, Ber. 10, 1068; Arends, Chem. Ind. 16, 78; Béhal and Choaz, Compt. rend. 109, 817; 110, 1270). It has remarkable antipyretic and analgesic properties. Other chloralimido compounds have been described by Moschelles (Ber. 24, 1803).

Chloralamide or chloral formamide $C_3H_4Cl_3NO_2$ is produced by gently heating chloral and formamide in molecular proportions (J. F. von Mering, Eng. Pat. 7391; D. R. P. 50586; J. Soc. Chem. Ind. 1890, 413). When recrystallised, it forms colourless crystals melting at 115°–116°; it is soluble in 9 parts of water, or in 1½ parts of 96 p.c. alcohol. It is without smell, and has a slightly bitter taste; when heated above 60°, it is decomposed; aqueous or alcoholic solutions are unaffected by weak acids or by silver nitrate, but are rapidly decomposed by alkali hydroxides, more slowly by alkali carbonates. As a hypnotic it has been proved superior to chloral hydrate, and is of most value in cases of nervous insomnia and similar disorders (Hagner and Hübner, Weiner Med. Presse, 1899, 1361). It has no corroding action, does not affect the digestion, nor disturb the heart. It may be taken internally as a powder, prepared by triturating 1–3 grams of the amide with 1 gram of fennel-oil sugar (*Ellæosaccharum Fœniculi*) (Merck's Bull. 1889, 85).

Chloralose $C_8H_{11}Cl_3O_6$ is obtained by heating equal parts of chloral and glucose, both anhydrous, on the water-bath. The vitreous mass is boiled with water to remove the chloral, and the concentrated aqueous solution deposits a crystalline compound, from which chloralose is extracted by alcohol. On treating the residue with ether, a compound isomeric with chloralose, termed *parachloralose*, is obtained. Chloralose

melts at 187°, and is a powerful hypnotic; whilst parachloralose melts at 227°, and possesses no hypnotic properties. By oxidising these compounds with nitric acid, followed by potassium permanganate, the corresponding chloralic acids are obtained; m.p. 212° and 202° respectively (Hanriot and Richet, Bull. Soc. chim. [3] 11, 37; 12, 303; Compt. rend. 116, 63; 122, 1127; 148, 1265; Meunier, *ibid.* 122, 142; Petit and Polonovski, Bull. Soc. chim. 3, [3] 861).

Chloral-acetonechloroform $C_6H_8O_2Cl_6$ is prepared by heating molecular quantities of chloral and acetonechloroform. It melts at 65°, and has a faint odour and taste resembling camphor (Hoffmann-Laroche, U.S. Pat. 778277; J. Soc. Chem. Ind. 1905, 150).

Chloral-bromal-carbamide is obtained by mixing urea with molecular quantities of chloral and bromal, or equivalent quantities of their hydrates in the presence of concentrated hydrochloric or sulphuric acid (Kalle & Co. D. R. P. 128462; Chem. Zentr. 1902, i. 547).

The following condensation products of chloral have been prepared: chloralacetone, chloralacetophenone, and chloraldol (Gigli, Gazz. chim. ital. 28, [2] 83; Königs, Ber. 1892, 792; 1893, 554; Wislicenus, Kircheisen, and Sattler, *ibid.* 1893, 908); carbonylchloraldehydes (Farb. vorm. F. Bayer & Co. D. R. P. 121223, Chem. Zentr. 1901, ii. 69); chloral nitrite (Bertoni, Gazz. chim. ital. 24, ii. 20); the compounds with aminoazobenzene (Betti, *ibid.* 28, 241); with amidooxybenzoic esters (Kalle & Co. D. R. P. 112216; Chem. Zentr. 1900, ii. 791); with aromatic hydrocarbons (Biltz, Ber. 1893, 1952; Dinesmann, Compt. rend. 1905, 141, 201); with hexamethylenetetramine (Lederer, Eng. Pat. 17693; J. Soc. Chem. Ind. 1897, 1039); with hydroveratine (Frankforter, Amer. Chem. J. 20, 358); with methylpropanoldialkamino- acids (Poulenc Frères & Fourneau, Fr. Pat. 382787; D. R. P. 203643; J. Soc. Chem. Ind. 1908, 246); with menthol and terpinol (Wagnitz, Eng. Pat. 19103; J. Soc. Chem. Ind. 1899, 856; Schmitt, Compt. rend. Soc. Biol. 1890, 678); and with resorcinol (Causse, Bull. Soc. chim. 3, [3] 861; Hewitt and Pope, Chem. Soc. Trans. 1896, 1265).

Polymerides. Two polymerides of chloral are known, an insoluble and a soluble substance. When pure, chloral is perfectly stable, but traces of impurities, and particularly of sulphuric acid (Byasson, Compt. rend. 91, 1071) convert it into *metachloral*, a white amorphous solid. It may be prepared by leaving chloral hydrate in contact with half its weight of concentrated sulphuric acid for several hours, until a pasty mass is formed. After pouring off the acid, the residue is introduced into a well-cooled solution of hydrochloric acid, and the product, which now becomes solid, is washed and dried over sulphuric acid. Chloral alcoholate may be substituted for chloral hydrate in this preparation (Gärtner, D. R. P. 170534; Chem. Soc. Abstr. 1906, i. 628). Another method is to add 7 parts of anhydrous aluminium chloride to 100 parts of well-cooled anhydrous chloral, the temperature being kept below 40°. In the course of an hour the whole mass solidifies. After 24 hours the hard mass is broken up, extracted with dilute hydrochloric acid, washed with alcohol, and dried at a moderate temperature (Erdmann, D. R. P. 139392; Chem. Zeit. 27, [20] 223). It is insoluble in alcohol, ether, water, and acids, but soluble in sodium carbonate solution. On warming with alcohol, it yields chloroform, and on distillation at 180°–250° is reconverted into chloral (Kolbe, Annalen, 54, 183 [footnote]). It is tasteless, and can be employed as an anæsthetic; unlike chloral hydrate, it has no irritating effect on the mucous membrane of the stomach.

The soluble polymeride is obtained by treating chloral with pyridine or any other amine in the cold, and then acidifying. It is a slightly volatile anæsthetic substance, volatilising without melting, converted by hot water or hot alcohol into chloral hydrate and chloral alcoholate respectively, and decomposed by alkalis into chloroform and formic acid. It is soluble in water (Gärtner, D. R. P. 165984; U.S. Pat. 768744; Chem. Soc. Abstr. 1906, i. 481).

Chloral hydrate $CCl_3{\cdot}CHO{+}H_2O$ or $CCl_3{\cdot}CH(OH)_2$.

Properties.—Chloral hydrate crystallises in monoclinic tables (Groth, Ber. 5, 676), and has a peculiar odour and sharp taste. Its m.p. is 57° (Meyer and Dulk, Annalen, 171, 75), 47·4° (Van Rossem, Zeitsch. physikal. Chem. 1908, 62, 681); b.p. 97·5°; and sp.gr. 1·818 (in powder) and 1·848 (crystallised) (Schröder, Ber. 12, 562). It dissolves readily in water, 1 part of water dissolving 4·7 parts of chloral hydrate at 17·5° (Mauch, Arch. Pharm. 240, 113), alcohol, ether, chloroform, turpentine, and light petroleum; and its solubility in carbon disulphide is given by Flückiger (*l.c.*) as 1 in 45 at 15°–18°, and 1 in 4·5 at the boiling-point. Concentrated sulphuric acid decomposes it into chloral and water, and alkalis act upon it as upon chloral. A modification of the hydrate, melting at 80°, is obtained by rapidly evaporating an acetic acid solution of anhydrous chloral over sulphuric acid (Meyer and Dulk, *l.c.*); this is probably the semihydrate described by Van Rossem (*l.c.*). Under the influence of light and air, chloral hydrate is decomposed, the decomposition products being hydrochloric acid and carbon dioxide or monoxide, or water, chlorine, and carbon dioxide, the amount of available oxygen determining the products (School and Van den Berg. Ph. Weekblad. 43, 42).

Chloral hydrate should be free from alcoholate, which has not the same physiological properties; and when warmed with twice its volume of water it should give a clear solution, free from oily drops and not precipitated by silver nitrate. When carefully heated, it should volatilise completely, and the vapours should not be inflammable; when gently warmed with 3 vols. of strong sulphuric acid the mixture should remain clear. On warming chloral hydrate with potassium hydroxide, turbidity is caused through the separation of chloroform; the clear portion is decanted, and iodine dissolved in potassium iodide added. So soon as the liquid begins to turn yellow, it is cooled, when the presence of alcohol and consequently of chloral alcoholate, is indicated by the formation of a precipitate of iodoform (Trillat, J. Pharm. Chim. 5, 218). Chloral alcoholate may also be detected by the Zeisel method for the estimation of ethoxyl (Schmidinge,

Monatsh. 21, 36). Chloral hydrate is converted into alcoholate when dissolved in alcohol, and similarly, chloral alcoholate is very slightly soluble in water, dissolving slowly to form chloral hydrate. Potassium carbonate is a good antidote to chloral poisoning, if it has not reached the blood (Klar, J. Soc. Chem. Ind. 1896, 555).

Physiological Action.—Compare Liebreich (Ber. 2, 269); Personne (Compt. rend. 78, 129); Byasson (*ibid.* 78, 649); Tomaszewicz (abstracted, Chem. Soc. Trans. 1874, 814); Tanret (J. Pharm. Chim. [4] 20, 355); and Trillat (*l.c.*).

Estimation.—4 grams of the sample are treated with 30 c.c. of normal caustic soda in a stoppered bottle, and shaken vigorously for a few minutes without the application of heat. On titrating back with normal sulphuric acid, using litmus as an indicator, 5·8 c.c. should be required for complete neutralisation (Alcock and Thomas, Pharm. J. 63, 236; and Sargeant, *ibid.*). Owing to the secondary reaction $CHCl_3+3NaOH=3NaCl+CO+2H_2O$, this titration with acid is slightly inaccurate. Modifications of the method have been devised by Trillat (*l.c.*); Hinrichs (Pharm. J. 70, 530); Desgrez (Compt. rend. 125, 780; Analyst, 23, 76); Self (Pharm. J. 79, 4); and Garnier (Chem. Zentr. 1908, i. 1492). Another method is to heat 0·3 gram of the sample with 1 gram of aluminium powder, or 2·5 grams of zinc filings, 15 c.c. of glacial acetic acid, and 40 c.c. of water under a reflux condenser for half an hour. The mixture is filtered and washed, and the chlorine estimated volumetrically or gravimetrically as silver chloride (Self, *l.c.*). Wallis (Pharm. J. 76, 162) treats the chloral hydrate with caustic soda in a bottle, and then estimates the chlorine as silver chloride. It may also be determined iodometrically (Rupp, Arch. Pharm. 241, [5] 326).

Chloral hydrate may be detected by means of the green colour formed on the addition of antimony trichloride to a solution in castor oil (Covelli, Chem. Zeit. 31, 342); or by the colours formed when it reacts with resorcinol in the presence of sulphuric acid (Jaworowski, Zeitsch. anal. Chem. 37, 60). Another method is to add a solution of ammonium sulphide, when a pinkish or yellow precipitate is obtained, and an oil having the odour of walnuts (Lesinsky and Grundlich, Amer. Chem. J. 19, 603). Chloral hydrate is valuable for extracting alkaloids from plants containing much resin, essential oils, &c. (Schaer, Zeitsch. anal. Chem. 38, 469); it is used in rubber analysis (Weber, J. Soc. Chem. Ind. 1903, 576); in microchemical investigations (Schaer, Chem. Soc. Abst. 1908, i. 62); and in qualitative analysis (Mauch, Arch. Pharm. 240, 166).

Derivatives.—**Chloral antipyrine** is obtained by the condensation of chloral hydrate with antipyrine (Béthal and Choaz, Ann. Chim. Phys. 27, 319).

Chloral caffeine is formed when chloral hydrate and caffeine are brought together in aqueous or alcoholic solutions in molecular proportions. It is recrystallised from warm water at 30°, and, owing to its easy solubility as opposed to the difficult solubility of caffeine, is of medicinal value (Chem. Fab. auf Act. vorm. E. Schering, D. R. P. 75847; J. Soc. Chem. Ind. 1895, 987).

Chloral tannin is prepared by the condensation of chloral hydrate with tannin in the presence of sulphuric acid. It is a greyish-brown amorphous powder, having valuable dermatological properties (Farb. vorm. Fried. Bayer & Co. D. R. P. 98273; Eng. Pat. 2882; J. Soc. Chem. Ind. 1899, 172).

Chloraldoxime is prepared by treating chloral hydrate (1 mol.) with hydroxylamine hydrochloride (4 mols.) and a little water; m.p. 39°–40° (Meyer, Annalen, 264, 116; Tarugi, Gazz. chim. ital. 21, ii. 6).

Chloralhydroxylamine is obtained by triturating molecular quantities of chloral hydrate, sodium carbonate, and hydroxylamine hydrochloride, dissolving the mass in a little water, and extracting with ether; m.p. 98° (Hantzsch, Ber. 1892, 701).

Compounds with formaldehyde are described by Pinner (Ber. 1898, 1926).

Chloral alcoholates. The preparation of *chloral ethylalcoholate* has already been described. It may also be obtained by the action of chloral on absolute alcohol (Martius and Mendelssohn, Ber. 3, 444). It crystallises in needles, melts at 44°–46° (Meyer and Dulk, Annalen, 171, 78), at 46° (Lieben, Ber. 3, 907); boils at 115°; is sparingly soluble in water, more soluble in absolute alcohol, 1 part of alcohol dissolving 4·4 parts of chloral alcoholate at 17·5° (Mauch, Arch. Pharm. 240, 113). Sulphuric acid decomposes it into chloral and alcohol. Chloral propylalcoholate, b.p. 120°–122°, and chloral *iso*propylalcoholate, m.p. 47°, and b.p. 108°, have been described by Gabutti (Gazz. chim. ital. 31, i. 86), and Vitoria (Chem Soc. Abst. 1905, i. 110); chloral amylalcoholate by Gradamer (Arch. Pharm. 243, 30), and Kalle & Co. (D. R. P. 115251; Chem. Zentr. 1900, ii. 1141). Other alcoholates have been prepared by Jacobsen (Annalen, 157, 224), and Kuntze (Arch. Pharm. 246, 91).

Butyl chloral $CH_3{\cdot}CHCl{\cdot}CCl_2{\cdot}CHO$; more correctly, tri-chlor-butyric-aldehyde; b.p. 164°–165° at 750 mm.; sp.gr. 1·3956 at 20°/4° (Brühl, Annalen, 203, 20). It is a colourless oil, having a characteristic chloral odour, formed by the action of chlorine upon ordinary aldehyde or paraldehyde (Krämer and Pinner, Ber. 3, 383). Chloracetaldehyde $CH_2Cl{\cdot}CHO$ is first formed, and this condenses with another molecule of acetaldehyde, forming *a*-chlorcrotonaldehyde $CH_3{\cdot}CH:CCl{\cdot}CHO$ and water, and this, by the action of more chlorine, forms the butyl chloral.

Preparation.—Chlorine is led through cooled paraldehyde (or aldehyde cooled by a freezing mixture); water is then added, and the liquid neutralised with calcium carbonate. The mixture is then distilled on the oil-bath in a current of steam, and the hydrate is thus obtained. This is then purified by recrystallisation from water, and decomposed by distillation in a stream of hydrochloric acid gas (Pinner, Annalen, 179, 26).

Butyl chloral is converted by fuming nitric acid into *aaβ*-trichlorbutyric acid. Phosphorus pentachloride converts it into a body $C_4H_4Cl_4$, which boils at 200°. It combines with zinc-ethyl to form a compound which is decomposed

by water with formation of trichlorobutyl alcohol.

The ammonia compound

$$CH_3{\cdot}CHCl{\cdot}CCl_2{\cdot}CH(OH)NH_2,$$

m.p. 62°, is formed by leading ammonia into a cooled mixture of 1 part of butylchloral, and 1½ parts of chloroform (Schiff and Tassinari, Ber. 10, 1783). It forms a solid mass, insoluble in water, soluble in ether, alcohol, and chloroform. Is readily decomposed on heating.

Butyl chloral has a strong affinity for water, and readily forms

Butylchloral hydrate $CH_3{\cdot}CHCl{\cdot}CCl_2{\cdot}CHO + H_2O$. This compound, which is also known as butyl chloral, is prepared by passing chlorine into paracetaldehyde (Freundler, Compt. rend. 143, 682). It forms white crystalline trimetric plates of a peculiar odour, with difficulty soluble in cold, more readily in hot water; very readily soluble in alcohol; m.p. 78°, with partial dissociation, and sp.gr. 1·694 (Schröder, Ber. 12, 562). For some years after its discovery in 1870, it was regarded as croton-chloralhydrate. It is decomposed by distillation into the chloral and water. Alcohol and potassium cyanide convert the hydrate into ethyl α-chlorcrotonate. Zinc and hydrochloric acid, or zinc-dust and water, produce mono-chlorcrotonaldehyde, and finally crotonaldehyde (Sarnow, Annalen, 164, 108). With acetic acid and iron filings, butyraldehyde, normal butyl alcohol, and crotonyl alcohol are produced (Lieben and Zeisel, Monatsh. 1, 840). It is a valuable anodyne in cases of neuralgia, facial rheumatism, periostitis, &c. The following composition is recommended: butyl chloral hydrate, 2–5 grams; alcohol, 10 grams; glycerol, 20 grams; and distilled water, 120 grams (J. Soc. Chem. Ind. 1889, 476; 1890, 889). It is frequently adulterated with the cheaper chloral hydrate, from which it may be distinguished by the following reaction: A solution of pyrogallol in pure 65 p.c. sulphuric acid gives, when gently and carefully warmed, a blue colour with chloral, a ruby colour with butyl chloral and a more or less violet-to-blue colour with mixtures of the two compounds. On addition of a large quantity of water, the blue colour obtained with chloral changes to yellowish-brown, and the ruby colour obtained with butyl chloral to a more or less deep-violet colour (Galbutti, J. Soc. Chem. Ind. 1894, 273).

Derivatives.—Butylchloralantipyrine, yellow crystals, m.p. 70°–71° (Calderato, Chem. Zentr. 1902, ii. 1387); butylchloraldoxime (Tarugi, Gazz. chim. ital. 21, ii. 6).

CHLORALUM *v.* DISINFECTANTS.

CHLORAMINE-BLUE, -GREEN, *v.* AZO-COLOURING MATTERS.

CHLORAMINE-YELLOW *v.* PRIMULINE AND ITS DERIVATIVES.

CHLORANIL *v.* QUINONES.

CHLORATE OF POTASH, SODA *v.* CHLORINE.

CHLORAZIDE. N_3Cl. A gas obtained by mixing solutions of sodium azide N_3Na, and sodium hypochlorite, and acidifying with acetic acid. Chlorazide is highly explosive, slightly soluble in water, and insoluble in caustic alkalis (Raschig, Ber. 1908, 4194).

CHLORAZOL-BROWN, -DEEP BROWN, -BLUE, -VIOLET *v.* AZO- COLOURING MATTERS.

CHLORETONE *v.* ACETONECHLOROFORM.

CHLORIDE OF LIME, POTASH, SODA *v.* CHLORINE.

CHLORINE. Symbol Cl. At. wt. 35·46. Chlorine was first obtained by Scheele in 1774 by the action of hydrochloric acid upon manganese dioxide, and was termed by him 'dephlogisticated marine acid air.' The idea that it was a compound substance prevailed until 1809, when Gay-Lussac and Thénard suggested that it was probably an elementary body, a supposition confirmed by the investigations of Davy in 1810 (Phil. Trans. 1811, 1, 32). Davy gave it its present name, from χλωρός, greenish-yellow, in allusion to its characteristic colour.

Chlorine is never found free in nature; it exists mainly in combination with sodium, potassium, calcium, magnesium, &c. Sodium chloride occurs as *rock salt* in large quantities in Galicia, Tyrol, Transylvania, Spain, and in England (particularly in Cheshire) (*v. Sodium Chloride*, art. SODIUM). Potassium chloride is found as *sylvine* (*q.v.*), and in association with magnesium chloride as *carnallite* $KCl{\cdot}MgCl_2,6H_2O$ (*q.v.*) in the salt-beds of Stassfurt. Other naturally occurring chlorides are *matlockite* $PbCl_2{\cdot}PbO$, *horn silver* AgCl, *atacamite* $Cu_2Cl(OH)_3$, *calomel* HgCl, &c. Ferric chloride Fe_2Cl_6 and sal ammoniac are occasionally found native as products of volcanic action. Alkaline chlorides are also found in considerable quantity in sea-water and in many natural waters.

Sodium and potassium chlorides are present in most animal secretions, and free hydrochloric acid is met with in the gastric juice. Many plants, especially those growing in proximity to the sea, contain notable quantities of chlorides.

The readiest mode of preparing chlorine for laboratory purposes consists in heating manganese dioxide with hydrochloric acid, or by heating a mixture of manganese dioxide, common salt, and sulphuric acid:

$$MnO_2+4HCl=Cl_2+MnCl_2+2H_2O.$$
$$2NaCl+MnO_2+2H_2SO_4=Cl_2+Na_2SO_4+MnSO_4+2H_2O.$$

Both these processes are used on the large scale for the preparation of chlorine (*v. infra*).

Many other peroxides and certain oxy- salts may also be used for the preparation of chlorine; thus red lead or potassium dichromate generate the gas when heated with hydrochloric acid.

$$Pb_3O_4+8HCl=Cl_2+3PbCl_2+4H_2O.$$
$$K_2Cr_2O_7+14HCl=3Cl_2+2KCl+Cr_2Cl_6+7H_2O.$$
$$KClO_3+2HCl=Cl+ClO_2+KCl+H_2O.$$

Chlorine is also formed when the heated vapours of nitric and hydrochloric acid react upon each other: $2HCl+2HNO_3=Cl_2+N_2O_4+2H_2O$.

Certain chlorides, *e.g.* $MgCl_2$, $PbCl_4$, $AuCl_3$, &c., evolve chlorine when heated in air.

(For other processes, *v. infra.*)

At ordinary temperatures and pressures chlorine is a greenish-yellow gas, which becomes darker in colour as it is warmed; under strong pressures the colour becomes orange-yellow. Even when largely diluted with air, the gas possesses a characteristic pungent and irritating smell; it cannot be respired, as it rapidly

attacks the membranes. The gas is incombustible in air, although it may be made to burn in hydrogen; ordinary illuminating flames, *e.g.* of coal gas, tallow, wax, &c., burn in chlorine with separation of carbon and formation of hydrochloric acid gas.

The sp.gr. of chlorine shows a gradual diminution up to 240°, when its density becomes normal, viz. 2·4502 (Jahns, Ber. 15, 1242).

40°	80°	120°	160°	200°	240°
2·4844	2·4776	2·4708	2·4641	2·4572	2·4504

The absorption spectrum of chlorine shows numerous dark lines in addition to complete absorption in the blue and violet.

Chlorine is readily liquefied to a dark greenish-yellow liquid of sp.gr. 1·33, b.p. −33·6°. It can be solidified at a low temperature. Liquid chlorine is not miscible with water; its refractive index is lower than that of water, and it is a non-conductor of electricity.

Chlorine gas is readily soluble in water, its absorption coefficient between 10° and 41·5°, according to Schönfeld (Annalen, 93, 26; 96, 8), is

$$3{\cdot}0361-0{\cdot}046196t+0{\cdot}0001107t^2$$

by means of which the following table showing the volume of chlorine at 0° and 760 mm. absorbed by 1 vol. of water at varying temperatures is calculated:—

10°	15°	20°	25°	30°	35°
2·5852	2·3681	2·1565	1·9504	1·7499	1·5550

(*v.* also Pickering, Chem. Soc. Trans. 1880, 139).

The volume of chlorine absorbed from a mixture of that gas with an indifferent gas, as hydrogen or carbon dioxide, is greater than that calculated from the law of partial pressures (Roscoe, Chem. Soc. Trans. 8, 14).

Chlorine acts as an active germicide on account of its affinity for hydrogen, and the consequent release of nascent oxygen when it comes into contact with micro-organisms in a moist condition. A summary of work done on gaseous chlorine as a disinfectant is given by Clayton (J. Soc. Chem. Ind. 1896, 320).

Chlorine-water has the characteristic smell and colour of the gas; in daylight, and especially when exposed to sunshine, it gradually loses its colour owing to the action of the chlorine on the water, the main reaction being

$$H_2O+Cl_2=2HCl+O.$$

On cooling a saturated solution to 0°, it deposits crystals of so-called chlorine hydrate of a light-yellow colour, which become almost white when cooled to −50°. By gently heating the crystals in a sealed tube, they are readily resolved into water and free chlorine, which may be thus obtained as a liquid.

Chlorine is an active chemical agent, and combines with many substances even at the ordinary temperature. Phosphorus ignites spontaneously in the gas, forming phosphorus trichloride, which, in contact with excess of chlorine, is ultimately converted into phosphorus pentachloride. Finely divided arsenic, antimony, copper, tin, lead, and iron burn in chlorine, forming the respective chlorides. Certain of these reactions are modified if the chlorine is absolutely free from moisture. Wanklyn (Chem. News, 20, 271) found that sodium might be melted in dry chlorine without action, although the metal readily burns in chlorine as ordinarily prepared. Cowper (Chem Soc. Trans. 43, 153) found that Dutch metal, zinc, and magnesium were unacted upon by dry chlorine; silver and bismuth were only slowly attacked.

Sulphur dioxide, ethylene, and carbon monoxide readily unite with chlorine. Chlorine rapidly attacks many organic substances, forming *addition products* as in the case of ethylene, or *substitution products* as in that of marsh gas. Chlorine has, indeed, a very strong affinity for hydrogen; a lighted taper plunged into an atmosphere of chlorine continues to burn with a dull lurid flame accompanied by much soot. If a piece of paper moistened with oil of turpentine $C_{10}H_{16}$ be thrust into a jar of the gas, it takes fire and burns with a cloud of smoke. By reason of its tendency to unite with hydrogen, chlorine acts indirectly as an oxidising agent in presence of moisture. Many metallic protoxides are converted into peroxides by the action of the gas in presence of water, the hydrogen of which combines with the chlorine to form hydrochloric acid, whilst the liberated oxygen attacks the metallic oxide. If a stream of chlorine is led into an alkaline solution containing sulphur, or a sulphur compound in solution or suspension, the sulphur, in presence of water, is rapidly oxidised by the nascent oxygen to the state of sulphuric acid. The oxidising action of chlorine is frequently made use of in chemical analysis. By virtue of its oxidising action, chlorine destroys many organic colouring matters, and is hence used directly or indirectly for bleaching.

Industrial Preparation of Chlorine.

Chlorine is prepared industrially by:

(*a*) The action of hydrochloric acid on substances capable of oxidising the hydrogen, thus setting the chlorine at liberty.

(*b*) The electrolysis of metallic chlorides.

(*c*) Chlorine can be prepared and has been prepared on the small industrial scale by the direct action of sulphuric acid on a mixture of sodium chloride and manganese peroxide. It is, however, usually obtained by the oxidation of the free HCl obtained by the decomposition of common salt with sulphuric acid in the manufacture of sulphate of soda.

The methods of oxidation adopted are:—

(1) By the action of MnO_2.

(2) By the direct action of atmospheric oxygen aided by the presence of a catalyst or carrier.

To deal with the oxidation by MnO_2 first.

The raw materials used are:

A solution of hydrochloric acid in water or muriatic acid usually obtained as mentioned above in the manufacture of sodium sulphate.

The solution used should be as strong as possible, because complete exhaustion of the acid by manganese peroxide is impracticable, and a residual liquor containing a considerable amount of unavailable acid is always left. The

stronger the hydrochloric acid solution to start with the smaller the percentage of the total HCl which is lost (for actual figures, *see* below).

The only impurity occurring in sufficient quantities in ordinary commercial hydrochloric acid to have any serious effect is sulphuric acid. The liquid hydrochloric acid obtained by condensation of the salt cake (sodium sulphate) roaster gas may contain anything up to 3 p.c. of sulphuric acid, and, as calcium chloride, is always present in the chlorine generators and in the final neutralising wells, calcium sulphate is thrown down in the form of a voluminous precipitate, which entails labour and expense in filter pressing and handling, and always results in loss of manganese.

Manganese ore (peroxide).—Originally, native manganese ore was the only form of peroxide used for the generation of chlorine from HCl, and it is still the source from which the manganese in use is actually derived. Formerly the solution of manganese chloride obtained by the action of HCl on MnO_2 was a waste product, and after neutralising with limestone dust was run away. The invention and working out of the 'Weldon' process enabled the manganese in these waste liquors to be cheaply recovered in the form of peroxide, and the manganese ore is now used in large scale manufacture only to make up the inevitable losses of the recovery process.

The manganese ore used for the generation of chlorine should contain a high percentage of MnO_2. The lower oxides of manganese also liberate chlorine, but only a smaller proportion of the total as shown by the following equations:—

$$MnO_2+4HCl=MnCl_2+2H_2O+Cl_2.$$
$$Mn_2O_3+6HCl=2MnCl_2+3H_2O+Cl_2.$$
$$Mn_3O_4+8HCl=3MnCl_2+4H_2O+Cl_2.$$

Pyrolusite is the manganese ore generally used. This mineral is found in rhombic prisms, usually occurring in distinctly crystalline masses of a fibrous structure; its sp.gr. is 4·7–5, and its colour iron-black to dark steel-grey with a metallic lustre. It is soft and soils the fingers.

The ore is widely distributed, occurring in Germany at Elgersburg, and Giessen, in Bohemia, Transylvania, Russia, India, Australia, Japan, and the United States of America.

The chief source of the industrial pyrolusite used in this country is Southern Russia.

The ore varies usually from 75 p.c. to 85 p.c. MnO_2.

An average analysis of the Russian ore is: 80 p.c. MnO_2; 1 p.c. MnO; 3 p.c. H_2O.

It is customary to buy and sell manganese ore on the percentage of MnO_2 only.

The higher the percentage of MnO_2, the more valuable the ore, as the impurities, even if substances such as $BaSO_4$ and SiO_2, do harm by coating the particles of MnO_2 and preventing the action of the HCl, and also by adding to the amount of waste material to be handled, filtered, washed, and deposited. If the impurities are carbonates ($CaCO_3$, $BaCO_3$, &c.), they not only waste hydrochloric acid, but the CO_2 evolved on their solution harms the bleaching powder into which the bulk of industrial chlorine is made.

The physical condition of the manganese is also important, the softer ores being preferable to the harder ones, which are more slowly acted on by the hydrochloric acid.

The manufacture of chlorine from manganese and liquid hydrochloric acid is carried out usually in 'stills' made of acid-proof stone, such as Yorkshire flag, and occasionally on a small scale in stoneware vessels. *Stoneware stills* can be made only of moderate size, and hence are mostly used for producing chlorine on a small scale, not for manufacturing bleaching powder. Fig. 1 shows one of the best-known forms of stoneware stills, intended for heating from the outside in a water- or steam-bath, made of wood or masonry. The manganese is placed in the perforated cylinder, which holds about 1 cwt., and is put in and out by means of specially shaped tongs, through the large opening. The small necks serve for introducing the acid and taking away the gas. At the end of the operation the still liquor is drawn off by a siphon, or by a discharge pipe passing through the steam-jacket. Since the acid is not diluted by steam-water, it is much better exhausted than in the large stone stills described below. Such small stills permit of careful and economical working so far as materials are concerned, and they necessitate hardly more labour than large ones.

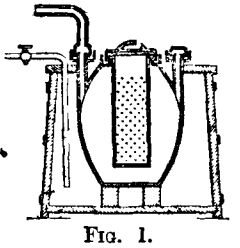


Fig. 1.

These stoneware stills are sometimes heated by blowing steam into them, but this plan cannot be recommended, as the above-mentioned advantage is thus sacrificed, and, moreover, such stills easily crack.

Fig. 2 shows a contrivance which allows the chlorine pipes and the main pipe to be instantly connected or disconnected, and which, at the same time, shows how stop-cocks can be dispensed with for such purposes. There is a Y-shaped lead pipe *a*, the upper arms of which are converted into hydraulic lutes by 'burning' an outer pipe, *bb*, on to them. The ends of the gas pipes, both that leading from the stills *c*, and that leading to the gas main *d*, are widened out into cups dipping into the water which fills the annular space at *b*.

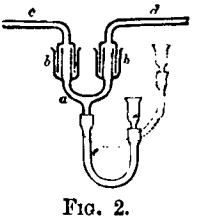


Fig. 2.

Stone stills must be made of silicious sandstone or other stone not acted upon by acids, and not liable to crack by rapid changes of temperature. Such stone is found at Southowram, and is known as 'Yorkshire flag.' A variety of stone superior to it in resisting changes of temperature is found at Heworth, near Newcastle-on-Tyne, but this requires boiling in tar for several days to make it impermeable to acids. In Germany there are also several stones adapted to this purpose, but none equals in excellence the volvic lava from the department of Puy-de-Dôme (France). This lava can be

had in thick blocks or thin slabs, and requires no boiling in tar to make it acid- and heat-proof.

It should be noticed that prolonged submersion in boiling tar is certainly an excellent way of toughening both stones and earthenware (fire clay), provided they possess a certain degree of porosity. It makes them resist both acids and changes of temperature, and at the same time hardens them very much, so that they must be worked into shape previous to the treatment.

Sometimes chlorine stills and acid tanks are hewn out of a block of stone (especially volvic lava); but this is a costly operation, and in case a single crack occurs, the whole vessel is lost. It is, therefore, more usual (in England universal) to build up chlorine stills (like acid tanks, condensers, &c.) from stone slabs joined in a suitable manner and held together by iron binders. Such a still is shown in Fig. 3, which represents it cut through in the middle. The bottom is formed by a stone, 10 to 12 inches thick, with grooves for the sides to fit in. The sides are stone slabs, 5 to 6, or even 8 inches thick, and joined at the corners either 'on the bevel,' or on the 'feather and groove' principle. In the former case the stones are all dressed in the same way, and are held together by cast-iron

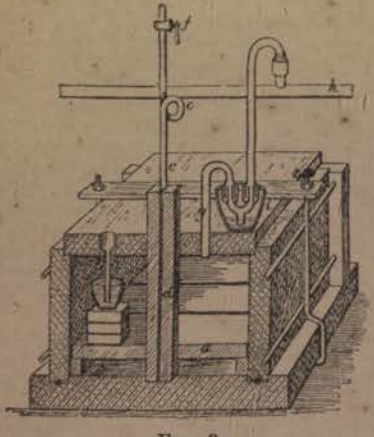


FIG. 3.

corner pieces, drawn together by long screw bolts; in the latter case, the end stones must project both ways over the sides, the latter fitting into grooves of the end stones (as is shown in the figure). The lid consists of one or more stones laid in a rebate. The joints are made tight by dressing a small groove into the two adjoining faces, and placing a §-inch india-rubber cord in the channel thus formed. Temporary joints, not intended to harden, can be made with a putty of linseed oil and china-clay.

The diagram shows how the still is fitted with the following parts. A false bottom *a*; a pipe *b*, for the introduction of hydrochloric acid, sealed at the bottom by the acid itself; a leaden steam pipe, *c*, connected at the bottom with a stone or stoneware steam column *d*, and at the top by the loop *e* with a tap *f* (the loop protecting the tap to some extent against the action of the chlorine); the earthenware or leaden gas pipe *g*, the connection of which with the gas main *h* can be opened or shut off at will by putting more or less water into the pot *i*. The man hole for charging the still and the discharging hole must be assumed to be provided in that half of the still not shown in the diagram.

These stills are made from 7×5×3 feet, inside measurement, and upwards.

Fig. 4 shows a still of the bevel-joint type,

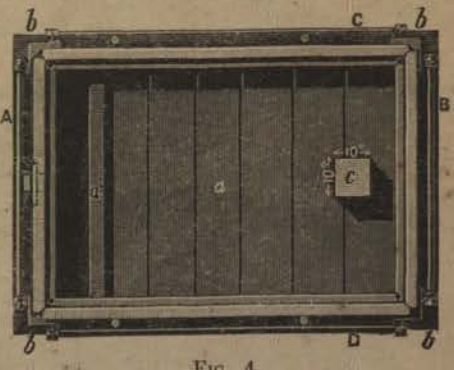


FIG. 4.

seen from above, with the cover removed; *a*, *a* are the flags forming the false bottom, one of which, *a'*, is made to stand up; *c* is the steam stone; A, B, C, D are the rods binding the stones together by means of the cast-iron corner pieces *b*, *b*.

In order to work the stills, those of smaller sizes, where the manganese is contained in a sieve, are usually first charged with the requisite quantity of acid. The sieve containing the manganese (about 1 cwt.) is then put in, the cover is at once put on and made tight by water-luting or cementing, and the evolution of chlorine begins forthwith. When it slackens, heat is gradually supplied by turning on the steam till the acid is exhausted. The stills are then allowed to cool down, usually till the next morning. They are then opened, the sieve is lifted out, the manganese remaining in it is washed and replenished by more ore, the liquor is siphoned or run out of the still, fresh acid is run in, and a new start can be made at once.

The large stone stills are cleaned out frequently, and are charged with from 6 to 10 cwts. of manganese broken up into pieces, which must be smaller in the case of hard ores, but should not be too small, lest too much is washed down below the false bottom. The still is then closed and acid is run in, at first quickly, afterwards gradually, so that it takes several hours to run in the full charge. All this time chlorine is given off, much heat being generated in the process, of course much more with concentrated than with somewhat dilute acid. When the evolution of gas becomes slow, steam is injected into the still, but very cautiously, as otherwise the water might be thrown out of the lutes, and only at intervals, for instance for 10 minutes every hour. Too much steaming causes too rapid an evolution of chlorine, and the volatili-

sation of much acid and water. The temperature of the stills ought never to get above 90°. It is preferable not to steam all the stills of a set at the same time, but in regular rotation, to produce a more continuous current of chlorine.

Chlorine stills ought to be kept going at least 24 hours, but large stills are better kept going for 48 hours, which will utilise more of the acid. Even then the liquid, when let out, emits an intolerable stench of chlorine, so that this operation is one of the most irksome, both for the workmen and those people who live near the works. Moreover, the 'still liquor,' even after being freed from its muddy constituents by settling, is one of the worst nuisances for any watercourse into which it may be run. In alkali works, all this nuisance has been completely overcome by the introduction of the Weldon process, where the still liquor from the fresh manganese ore is run into the Weldon stills instead of into the drains. At other works where chlorine is made on too small a scale to permit of applying the Weldon or other modern processes, the still liquor ought to be collected in a closed tank, and neutralised by chalk before running it away, even in a very diluted form.

The chlorine evolved in the stills is always contaminated with hydrochloric acid and water. For most purposes these must be removed as far as possible, which is done by conveying the gas in a long string of earthenware or lead pipes, externally cooled by air (or, if needful, by water), so that the water along with the acid condenses into a liquid.

The first reaction taking place in the chlorine stills is: $MnO_2+4HCl=MnCl_4+2H_2O$ or (more probably) $2MnO_2+8HCl=Mn_2Cl_6+4H_2O+Cl_2$. (There is some discrepancy of opinion as to which of these two chlorides of manganese is formed. Compare W. W. Fisher, Chem. News, 37, 250; U. S. Pickering, *ibid.* 39, 225; Berthelot, Compt. rend. 91, 251.)

These chlorides, $MnCl_4$ and Mn_2Cl_6, form a dark-brown solution which quickly decomposes even at the ordinary temperature into $MnCl_2$ and free chlorine, so that the ultimate result is: $MnO_2+4HCl=MnCl_2+2H_2O+Cl_2$; but this reaction is only completed at about 100° and with a certain excess of hydrochloric acid. Theoretically for $100MnO_2$, or an equivalent quantity of manganese ore, almost exactly 170 dry HCl=530 acid of 32°Tw., ought to be consumed; practically, at least, 10 p.c. more is used, and with low-strength acid, hard manganese, direct steaming, &c., twice the theoretical quantity of acid may be consumed.

Still liquor and the processes carried out for utilising it.—The waste liquor run from the stills contains chiefly manganous chloride, ferric chloride, the chlorides of other metals present in the ore, free hydrochloric acid, and a little chlorine.

Black's analysis of still liquor from ordinary stone stills, in a well-conducted works, shows how incompletely the acid is utilised there:

HCl	= 6·6220 = 6·622	p.c. HCl
Al_2Cl_6	= 0·6200 = 0·500	,, ,,
$MnCl_2$	= 10·5700 = 6·120	,, ,,
Fe_2Cl_6	= 0·4551 = 0·310	,, ,,
H_2O	= 81·7329	
	13·552	

Even if all the Mn had been originally present as MnO_2, only an equal quantity of HCl to that found as $MnCl_2$ (6·12) had escaped as chlorine, so that there was originally

$$13·552+6·12=19·672\ HCl$$

present. Accordingly, the HCl usefully employed was only 62·2 p.c.; that combined with Fe and Al, 4·1 p.c.; that found uncombined, 33·6 p.c. of the whole.

The free acid is tested for in daily practice by a very simple plan. To a measured volume of still liquor, standardised caustic soda liquor is run in from a burette till the formation of flakes of $Fe_2(OH)_6$, which do not dissolve on shaking, indicates the saturation of the free acid.

In small manufactories, where the scale of work does not permit the economic introduction of the Weldon process for the recovery of the manganese from the still liquors, the liquors have to be neutralised with limestone dust and run down the drain.

Of the many processes suggested before the Weldon process to overcome this difficulty and this loss of manganese, only the Dunlop process deserves mention. The Dunlop process was patented in 1855, and has been practised at St. Rollox for 30 years or more with great success. It consists in removing the free HCl and Fe_2Cl_6 by agitating the liquor with ground chalk (exactly as in the Weldon process), pumping the neutral solution of $MnCl_2$ and $CaCl_2$ into large horizontal cylinders fitted with agitating gear, mixing it with the quantity of ground chalk required for converting the $MnCl_2$ into $MnCO_3$, and producing this conversion by agitating under a steam pressure of 2–2½ atmospheres. The precipitate of $MnCO_3$ is settled out, washed, pressed, partially dried, and then oxidised by being exposed to a current of air in an oven heated to about 300° which is always kept moist. In 24 hours the process is complete. The paste is now found to consist of 67 p.c. MnO_2, 16 p.c. MnO, and 16 p.c. $CaCO_3$. This process is only remunerative where fuel is cheap, and as it requires very costly plant, it has never spread beyond the place of its origin, where it has also at last had to give way to the Weldon process, and is now only employed for the production of an artificial oxide of manganese for glassmaking.

The Weldon process for recovering Manganese.—The process bearing the above name has, like most other important inventions, been perfected by many successive improvements. Many of its features had been foreshadowed by former inventors; but without the indomitable energy of the late Walter Weldon, and the efficient practical help rendered to him at Messrs. Gamble & Co.'s works at St. Helens, it would have remained futile, like all its predecessors. Weldon's first attempts were made in 1866; in 1869 chlorine was first actually manufactured by Weldon mud. By carefully studying all the conditions of the reaction on the large scale, at last all obstacles were overcome and the fullest practical success was secured. This achievement alone entitles Mr. Weldon to be called one of the greatest benefactors to chemical industry.

The leading idea of the Weldon process is the following. We start with a solution of

manganous chloride—*i.e.* ordinary still liquor. This is deprived of free acid and ferric chloride by agitation with calcium carbonate under ordinary atmospheric pressure. To the neutral settled solution of $MnCl_2$ and $CaCl_2$ is added milk of lime more than sufficient for precipitating all manganese as $Mn(OH)_2$, so as to leave 33 p.c. to 40 p.c. lime in excess, both lime and manganous hydrate being partly suspended and partly dissolved in a solution of $CaCl_2$. This mixture is treated with a strong current of air, at a slightly raised temperature, when the oxygen acts upon it, forming principally a compound of MnO_2 and CaO. By adding a further quantity of $MnCl_2$ and blowing in more air, the proportion of CaO is reduced, the ultimate limit in ordinary cases being a compound of $1CaO$ with $2MnO_2$. The oxidation is now stopped; the thin paste or mud is run into tanks, where it separates into a thicker mud and a supernatant clear solution of $CaCl_2$. The latter is run to waste; the former, now called 'recovered manganese' or 'Weldon mud,' is still liquid enough to be run into a special kind of still, where it is decomposed by hydrochloric acid, yielding chlorine gas and a mixed solution of $CaCl_2$, $MnCl_2$, and a little uncombined HCl (much less than in the old process of working with native ore). This solution serves again as the starting-point for the recovery of MnO_2 in the way just described.

Long before Weldon's patents existed, it had been, of course, known that precipitated manganese protoxide could be more highly oxidised by means of atmospheric air. But Weldon was the first to find out that oxidation of MnO to MnO_2—a compound of distinctly acid properties—can only take place in the presence of a base which combines with it at the moment of its formation. If the only base present be $Mn(OH)_2$, then the MnO_2 will combine with it to form either MnO,MnO_2 or else $2MnO,MnO_2$, according to the temperature. Thus, when MnO is the only protoxide present, one half of it at most can be oxidised into MnO_2, the other half being required to *furnish* the necessary base for combining with MnO_2. If, however, another soluble protoxide be present, the MnO_2 combines with this instead of with MnO. The only other protoxide practically available is lime, which is sufficiently soluble in a solution of calcium chloride. If instead of MnO,MnO_2, we produce CaO,MnO_2, there is, of course, no advantage gained with respect to the consumption of acid, since in either case 6HCl are required to liberate 2Cl. But the advantage lies in this, that the absorption of oxygen by $Mn(OH)_2$ in the presence of dissolved lime is much more rapid than in the absence of a soluble base. The product of oxidation of $Mn(OH)_2$ by itself would be much more costly than native manganese.

It is not possible to employ a full equivalent of lime to each of $Mn(OH)_2$, so as to form $CaMnO_3$, because there cannot be present sufficient $CaCl_2$ to hold it in solution. Hence only enough $Ca(OH)_2$ is used to convert 0·6 of the Mn into calcium manganite, the other 0·4 of the manganese present is converted into manganite of manganese, $MnMnO_3$.

When thus 60 equivalents, $CaMnO_3$ and 40 $MnMnO_3$ have been formed, a further quantity of neutral solution of $CaCl_2$ and $MnCl_2$ ('final liquor') is mixed with it, and the injection of air is continued. At the temperature employed, $MnCl_2$ can act upon half of the lime of $CaMnO_3$, forming a compound of one CaO with two MnO_2, and $Mn(OH)_2$, which is, at the same time, oxidised to Mn_3O_4 or Mn_2O_3. The final product is a thin black mud, consisting of a solution of $CaCl_2$, holding in suspension a mixture of manganites of manganese with an acid manganite of calcium, and containing about 2·5 lbs. MnO_2 per cubic foot.

The following is the description of a Weldon plant. On the diagram, Fig. 5, D, D are the mud stills, of which there should be three or four, and which will be described in detail hereafter. There is, besides, an ordinary still, E, which serves for dissolving native manganese ore, to make up for the loss in recovery, and which is so fixed that its waste liquor can be discharged directly into one of the mud stills. G, G are the neutralising wells into which the manganese liquor from D, D is discharged, and where it is mixed with ground chalk or limestone dust by means of the agitator F, in order to remove the free HCl and the iron. H is a cast-iron pump with gun-metal piston, valves, &c., which forces the neutralised liquor into the chloride of manganese settlers A, A. The suction pipe, which dips in the acid liquor, is very quickly corroded unless it is made to turn on a swivel so as to lift it out before running acid liquor into the well. The settlers A, A (of which there must be at least two, or better, more) are made of wrought iron, which is only slightly acted upon by the neutralised liquor. In one of these tanks the muddy liquor is allowed to settle while the other one is being filled. They are provided with cocks or valves, continued inside into swivel pipes or india-rubber tubing, by which the liquor can be run off from any part of the tank without disturbing the sediment. The discharge pipes unite outside in an iron pipe, which divides again into two branches, one for each of the two oxidisers B (only one of which is shown here), into which they enter at about two-thirds or three-fourths of their height. Each settler also has a large bottom valve for removing the mud from time to time, by means of the pipes *g*, *g*.

If the settlers A, A are each $18 \times 12 \times 6$ feet, they hold, when full, about 40 tons apiece and weigh altogether upwards of 100 tons. They must, therefore, be very firmly mounted on a strong timber framework of 12- or 14-inch beams, resting on the same foundation as the manganese mud settlers.

The oxidisers B, in which the recovery proper takes place, are wrought-iron cylinders open at the top, with a flat bottom, fixed at such a height that there is sufficient fall for the manganese mud into the settlers C, C, and from these again into the stills D. They are charged with settled $MnCl_2$ liquor from A, A to rather more than half of their height, and with milk of lime directly from the tank J by the pump K. The 7-inch pipe *d* conveys compressed air (furnished by the blowing engines and the air-vessel *m*) into the oxidisers; it is carried over the top of B down to the bottom, and there branches out into a cross of pipes *n*, perforated with a number of holes for dividing the current of air. Each oxidiser also has a 2-inch steam

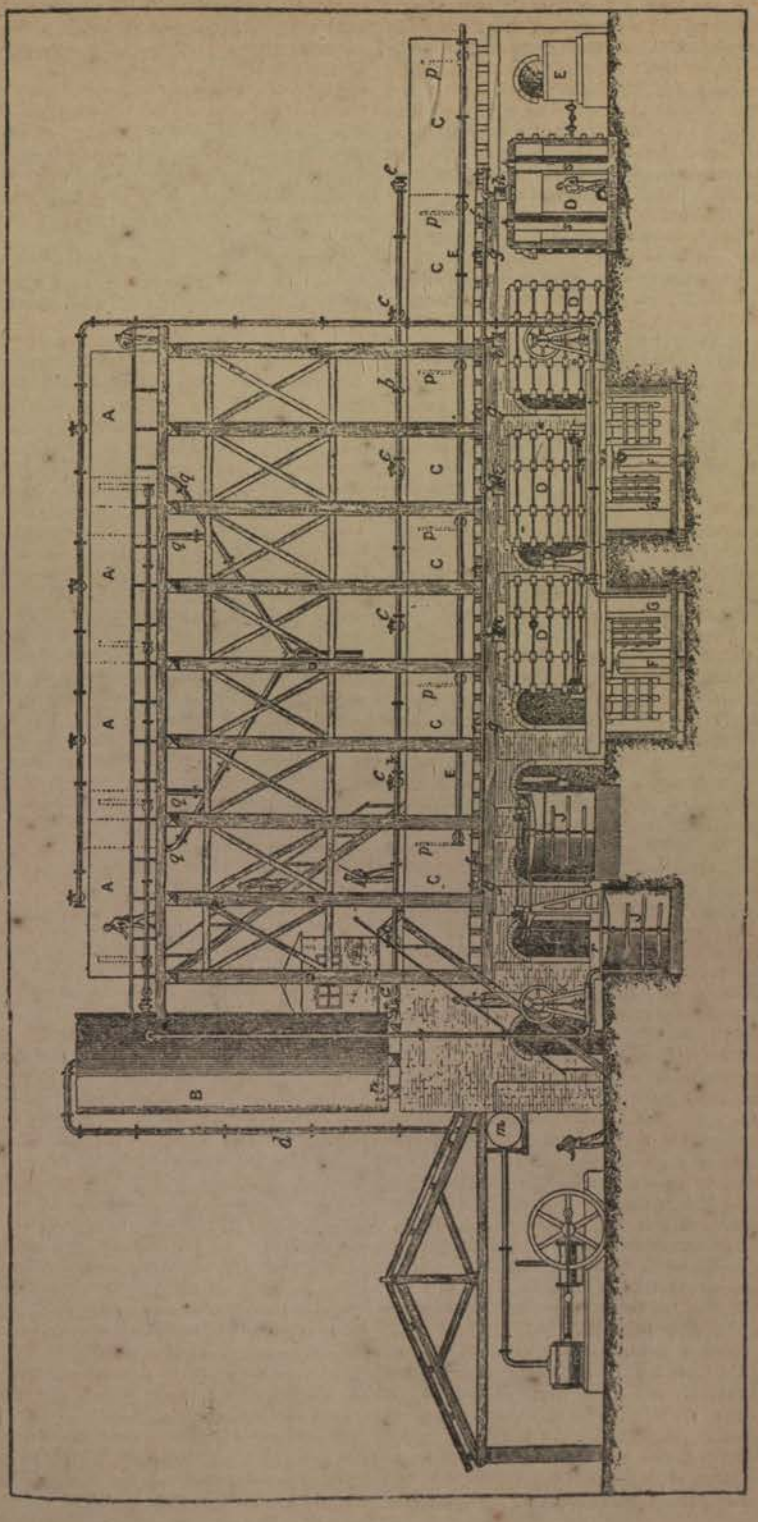


Fig. 5.

pipe (not shown here) which equally passes over the top down to the bottom and there branches out into a perforated cross. None of the pipes is directly connected with the shell of B, as the shaking during the blowing would loosen the joints; the only fixed connection which cannot be dispensed with is the $MnCl_2$ liquor pipe from A, A. It is usual to make the joints on this pipe with indiarubber rings to give a certain amount of elasticity. Lastly, there are discharge valves *a*, connected with a common pipe, *b*, which sends out a branch with 4-inch valves *c*, *c* over each mud settler C, C. These mud settlers, of which there must be at least four, better six, are fitted with 2-inch swivel pipes *p* for running off the $CaCl_2$ liquor, communicating with a pipe or shoot, *e*, leading to a catch-well, and at the bottom with a 4-inch pipe, *f*, with sluice valves *g*, *g*; from which each of the stills D, D is fed by a pipe and sluice valve *h*.

The engine is here shown as a horizontal twin-engine. For each ton of bleaching powder made, 100,000–150,000 cubic feet of air are required.

The milk of lime is made in the two iron cylinders J and J', each about 6 feet high and 7 or 8 feet wide; J serves for slaking the lime and preparing the milk, J' for storing it and supplying it to the lime-pump K. A donkey-engine bolted to J drives the agitators of both cylinders. J has a perforated cage in which the quicklime is put in order to be slaked by the water contained in the cylinder, and a door is secured to the cylinder in line with cage bottom in order to clean out unburnt lime.

The neutralising wells G, G are sunk in the ground, and are surrounded by puddled clay. They are made of large stone slabs in an octagonal shape, or of freestones in a circular shape, always, of course, so as to be altogether acid-proof. It is most important that there should be no loss of liquor from this well.

The chlorine stills belonging to this plant (*Weldon's stills* or *mud stills*) are very much larger, especially much higher, than the ordinary manganese-ore stills. The shape usual at small works is of square section about 7 feet ×7 feet, and 8 or 9 feet high. For large works, they are made octagonal (as shown in Fig. 5, and more in detail in Figs. 6 and 7), sometimes 12 feet wide and high. The bottom is made in two pieces, held together by corner brackets and bolts *a*, *a*. The sides, also in two tiers, are joined in the corners by indiarubber cords or bands; they are bound together by the brackets *b*, *b* and screw bolts, or by cable chains, drawn up tight by coupling screws, and pressing on wooden posts outside of the still sides. The cover is usually made dome-shaped. We note the funnel for manganese mud, *d*, the steam stone *c* resting in the socket *k*, the discharge cock *f*, the gas pipe *l*, the acid-supply pipe *e*, about half-way up the height of the still. There must be also a man hole, a stoneware cock with a glass tube for a liquor gauge, and a small testing cock, all of them not shown in the diagram.

We shall now describe the round of operations, beginning with the running of spent liquor from the mud stills into the neutralising well. The latter should be covered over, a pipe leading the gases (never free from chlorine) into a high chimney—if necessary, through a milk of lime tower. The liquor is here neutralised with ground chalk or limestone dust, of which no more than is absolutely necessary should be employed. This is best effected by grinding the calcium carbonate with water (or preferably with still liquor itself) into a milk, and running this in, with constant agitation, till no more CO_2 is given off and till there is no more acid reaction upon litmus paper. This operation will remove the free HCl and the Fe_2Cl_6, causing a precipitate of $Fe_2(OH)_6$; but $MnCl_2$ is not acted upon here. G. E. Davies proposed to utilise the base in the Weldon mud for the neutralisation of the free acid in the still liquor. This is done by adding to the still liquor, after it has dissolved as much manganese peroxide as possible, an excess of Weldon mud. The free acid left, though it will not attack the manganese peroxide, readily dissolves the CaO in the base. As the base has, in any case, to be dissolved in the acid, its use for neutralising the free acid left in the still liquor is a direct saving of acid. The saving made is equal to about 0·45 cwt. salt per ton of bleach for every gram per litre HCl so neutralised in the still liquor.

The neutralised liquor, along with all the mud, is now pumped into the liquor settlers at the top of the timber staging, where it must be completely clarified before being run into the oxidisers. Any matter remaining in suspension greatly interferes with the recovery process, and especially causes very troublesome frothing in blowing. The muddy deposit remaining in the settlers is run off from time to time through the bottom valve. This deposit formerly caused the principal loss of manganese in the Weldon process, by mechanically keeping a quantity of $MnCl_2$ in suspension and wasting it. But this can be avoided by removing the $MnCl_2$ from that deposit as much as possible, either by systematic washing or by a filter press, and reintroducing this $MnCl_2$ into the process. It is, of course, desirable to keep the bulk of the deposit as small as possible by not employing more calcium carbonate than is really necessary, and by employing hydrochloric acid containing very little sulphuric acid, which by the formation of $CaSO_4$ increases the bulk of the insoluble matters. Principally by attending to a thorough exhaustion of this settler mud—of course, together with carefully attending to all other manufacturing details—the consumption of fresh manganese ore, which at first often amounted to 10 p.c. of the weight of bleaching powder made, has in the best works been brought down to 2½ p.c.

The clarified liquor drawn off from this deposit is essentially a solution of MnCl and $CaCl_2$. The latter is not merely an accidental admixture, but it is absolutely necessary to the success of the process that the proportion of $CaCl_2$ to $MnCl_2$ should not fall below 1 to 2. This seems to be owing to the circumstance that a solution of $CaCl_2$ keeps much more $Ca(OH)_2$ in solution than water, in the shape of an oxychloride, and that this is necessary to expedite the subsequent reactions. The manganese chloride, contained in normal still liquor, corresponds to about 3½ lbs. MnO_2 per cubic foot.

The liquor is run into one of the oxidisers

till this is rather more than half full; the other half serves for containing the milk of lime, the 'final liquor,' and, above all, the froth formed during the operation.

While one of the oxidisers is being charged and heated up, the other one is under blast, so that the operation is a continuous one. The liquor must be heated to 55° by blowing in steam, but, when continuously working, it often has that temperature to begin with, at least in summer, owing to being heated in the stills.

The next operation is adding milk of lime. The lime employed for the Weldon process should be as pure as possible, and ought especially not to contain more than 1 p.c. of magnesia. It ought to be particularly well burnt and slaked, and completely separated from unburnt or unslaked (dead) particles by being strained through a fine wire mesh. Those particles cannot aid in the recovery of MnO_2, and they remain in this as injurious 'base.' The slaking takes place by directly introducing the quicklime into hot water, throwing it into the cage within the vessel J (Fig. 5), and agitating all the time. The coarser impurities remain behind in the cage, the finer ones in a drainer interposed between J and J'. The finished milk of lime in J' contains from 20 to 22½ lbs. of CaO per cubic foot, and is pumped either directly into the oxidiser or into the top cistern, from which it can be let down in a preferably regular stream, provided that it is kept agitated in that cistern itself (*cf. supra*).

In order to begin an operation, one of the oxidisers is half-filled with well-settled $MnCl_2$ liquor (of which a stock must be in reserve for 'final liquor'), and is heated to 55°. The blast is put on slowly, and milk of lime, of which the initial level in the store tank has been carefully noted, is run in till all manganese has been

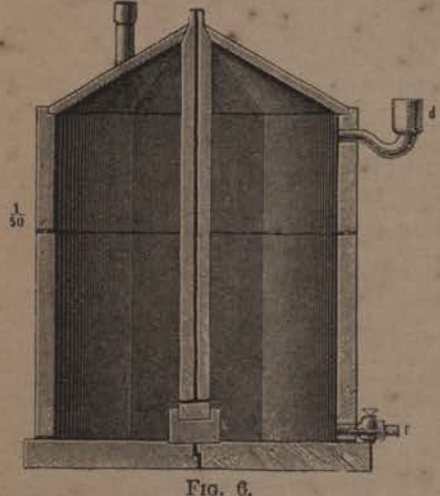


FIG. 6.

precipitated as $Mn(OH)_2$. This point is ascertained by frequent testings, both by trying whether red litmus paper turns blue (from an excess of lime), and by filtering a small sample and ascertaining by the addition of strong bleach liquor whether the filtrate turns brown in consequence of containing some $MnCl_2$. When this reaction ceases, the flow of lime is at once stopped, and the quantity consumed so far is read off on a gauge. This is merely done to be able to fix upon the further quantity of lime, which ought to be from 33 p.c. to 40 p.c. of that first used. The exact quantity of excess lime to be used must be ascertained at each works by independent trials, as it varies according to the nature of the raw materials, &c.

The 'excess lime' is run in immediately after the first, and the blast is at once put on with full strength; otherwise a 'thick batch' would be produced, whilst a 'red batch' (containing Mn_3O_4) is formed when the blast is put on too soon. The oxygen contained in the blast

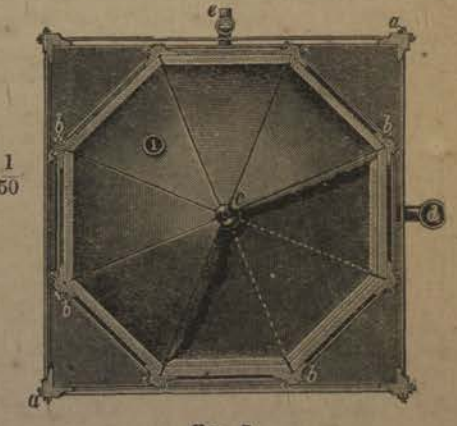


FIG. 7.

now acts upon the mixture of manganous and calcium hydroxides, and forms a manganite of calcium $CaMnO_3$, along with manganite of manganese Mn_2O_3. This means that at this stage each molecule of MnO_2 is combined with a full molecule of 'base,' either CaO or MnO. This amount of base must be reduced, otherwise too much acid is consumed, all the more so as the base is augmented by the $CaCO_3$, and Fe_2O_3 present as impurities, since the base must first be saturated before the MnO_2 can be acted upon. Although there is no theoretical impossibility against it, there seems to be no practical way of getting the base below 0·5 equiv., or even quite down to that point; 0·6 is considered very good, and 0·7 is the more usual amount.

With 0·7 of base, the Weldon mud consumes 5·4HCl for each 6HCl that would be required for Mn_2O_3; pure MnO_2 would only require 4HCl, but native manganese ore practically requires more acid than Weldon mud, in spite of the base of the latter, because it is so much more difficult to dissolve.

It is, however, not possible to arrive at a proper result by the simple blowing of air into the mud of calcium and manganous hydroxides. With 0·6 equivalent of excess of lime, the degree of oxidation obtained is usually about 86 p.c., the product before the addition of 'final liquor' consisting of 0·14 equivalents of MnO_2 combined

with 0·14 MnO, 0·48 MnO_2 with 0·48 CaO as $CaMnO_3$, and 0·24 MnO_2 with 0·12 CaO as $CaMn_2O_5$. There is thus 0·74 total protoxides to 0·86 MnO_2, or 0·86 equivalents of base per 1 equivalent of MnO_2. In order to reduce the base, some more chloride of manganese liquor is run in ('final liquor'), up to the point that a filtered sample gives the reaction for $MnCl_2$. In this case 0·4 eq. of $MnCl_2$ will have been used, taking away half of the lime in the 0·48 eq. $CaMnO_3$. If the blowing in of air is now continued until the absorption of oxygen ceases, the 0·24 eq. of $MnCl_2$ added will have been converted into Mn_3O_4 or Mn_2O_3, according to temperature. In the former case, the base will be reduced from 0·86 to 0·7, but at the same time the average degree of oxidation from 86 to 75·8 p.c.; in the latter case, the base will be 0·632, the degree of oxidation 79 p.c.

It should be noticed that these calculations only refer to the *combined* base, but do not include MgO, $CaCO_3$, Fe_2O_3, &c., which must be included in the ordinary method of testing for *total* base. With good work the total base does not exceed 0·7.

In actual practice, it is not possible to add the lime exactly as indicated by theory, for when the bleaching powder reaction in the filtered sample has ceased, decidedly more than 1 eq. of CaO has been added to 1 of $MnCl_2$, $Mn(OH)_2$ being soluble to a certain extent in $CaCl_2$; nor do all the molecules of lime instantly act upon $MnCl_2$, but they will do so afterwards. Actually from 1·1 up to 1·45 eq. of CaO is used at first, and this is brought up to 1·6 by the 'excess lime.' With that quantity a well-settling mud is obtained, from which a good deal of $CaCl_2$ solution can be drawn off, thus obtaining stronger manganese mud for the stills. Usually 12 cwts. of lime per ton of bleaching powder are required for the recovery process (*i.e.* about as much as in the bleaching-powder chambers).

The operation of blowing is carried out in this way. Tests are taken from time to time; it is ascertained whether the alkaline reaction continues, which ought to be the case perceptibly for at least an hour after the commencement of the blowing; also, whether the oxidation proceeds any further or not. When the latter is the case, some more $MnCl_2$ liquor is run in, without stopping the blast, until a filtered sample yields the brown reaction with bleach liquor. After a few minutes this reaction ceases, all dissolved $MnCl_2$ having been precipitated. Then a little more final liquor is added, and the blowing is continued, and this is repeated till it takes a somewhat long time to 'blow out' the manganese, which must be done before running the batch into one of the settlers.

It has been found preferable to apply a very strong current of air by means of a powerful blowing engine; in this way the work is not merely done in much less time, but with a smaller absolute amount of air than with smaller engines. The time should not exceed 5 hours, nor the quantity of air 150,000 cubic feet per ton of MnO_2. With very deep oxidisers even better results can be obtained.

The manganese mud, as it runs from the oxidisers, must be concentrated before entering the chlorine stills, since it would otherwise become indefinitely diluted by the acid, the milk of lime, &c. This is done by allowing it to remain some time in the mud settlers at the base of the oxidisers, where in a few hours it separates into a thicker mud and a clear solution of $CaCl_2$. The latter is run off by means of a swivel pipe, and before running into the waste drain it is made to pass through a catch well, where any MnO_2 carried away may be saved. The thicker manganese mud remaining behind, containing upwards of 6 lbs. MnO_2 per cubic foot, is still liquid enough to be run in pipes and through sluice valves into the chlorine stills.

The working up of the manganese mud takes place in this way. First, a charge of hydrochloric acid is run into the still, say 2 feet deep; in lieu of part of this, still liquor from native manganese ores may be employed. Then manganese mud is run in slowly by means of a sluice valve. Since in this fine state of division the action between MnO_2 and HCl is practically instantaneous, a perfectly uniform current of chlorine can be obtained by regulating the flow of manganese mud. When the liquid taken out at the test cocks begins to assume a dark colour, a little steam is blown in. The end is reached when the liquor, in spite of a sufficient temperature, is clear but coffee-coloured, and on pouring upon chalk produces only a slight effervescence. It ought not to contain more than about 1 p.c. of free HCl, if tested like ordinary still liquor (*cf. supra*). If the saturation of the HCl is driven too far, there is danger of some MnO_2 remaining behind, and getting lost with the mud from the $MnCl_2$ settlers. Each operation in the stills lasts from 4 to 6 hours; the liquor is then run into the neutralising well, and the round of operations begins anew.

The yield of chlorine by the Weldon process is mostly expressed in terms of the quantity of the salt required to be decomposed for manufacturing 1 ton of 37 p.c. bleaching powder.

In actual practice the quantity of salt used varies with the efficiency of the manufactory from 45 up to 70 cwts. salt per ton bleaching powder. As the quantity of chlorine (8 cwts.) required to make 1 ton of strong bleaching powder is actually contained in 14·2 cwts. salt (93 p.c. NaCl), the yield of chlorine in the Weldon process is under the best conditions less than 32 p.c.

Chlorine Processes employing Atmospheric Oxygen for the Liberation of Chlorine.

The Deacon Process.—After many unsuccessful attempts made by Oxland (1840), Jullion (1846), Binks (1860 and 1862), Dufrené (1865), and others, the labours of H. Deacon and F. Hurter, in the years from 1868 on, produced an entirely successful chlorine process which is founded on the direct oxidation of the H in HCl by atmospheric oxygen, and which utilises much more of the HCl than any process employing either native or recovered MnO_2. Some processes patented after theirs (Henderson, 1871; Weldon, 1871; Wigg, 1873, &c.) proceed on the same lines, but have not been practically successful.

The Deacon process starts from the well-known fact that a mixture of hydrochloric acid and oxygen at a certain temperature, especially

in contact with porous substances, partially changes into chlorine and water:

$$2HCl+O=H_2O+Cl_2.$$

This decomposition is very much assisted by the employment of substances which serve as oxygen-carriers, and of these the salts of copper (previously employed by Vogel, 1855; Gatty and Laurent, 1860; Mallet, 1866), have been found most useful. Probably in all cases cupric chloride is formed, which at once splits up into cuprous chloride and free chlorine. The Cu_2Cl_2 combines with oxygen to form oxychloride $CuO{\cdot}CuCl_2$, and this acts again upon HCl, yielding water and reforming cupric chloride, so that the reactions can begin over again:

$$(1)\ 2CuCl_2=Cu_2Cl_2+Cl_2.$$
$$(2)\ Cu_2Cl_2+O=Cl—Cu—O—Cu—Cl.$$
$$(3)\ Cu_2OCl_2+2HCl=H_2O+2CuCl_2.$$

Theoretically, *all* the HCl would thus be converted into chlorine, but in practice, under the best conditions, about two-thirds of this decomposition is effected. The undecomposed HCl is, however, not lost, but is recovered and can be utilised for other purposes, *e.g.* for the Weldon process.

From a diagram constructed by Hurter, showing the affinity of technically available elements for oxygen, chlorine, and hydrogen, it appears that no other metal than copper forms two oxides and two chlorides, in which the combination is of so loose a character. It is therefore almost a certainty that a cheaper and equally efficient catalyst cannot be found, and that the Deacon process is the best for the direct conversion of gaseous HCl into free chlorine.

Deacon's process deals with the gaseous hydrochloric acid, as it is evolved in decomposing common salt by sulphuric acid without condensing it into liquid acid. This is evidently a great advantage in one way, but when the salt cake is made in the ordinary hand-worked pot and furnace, it has the drawback that in the beginning of each operation much more HCl, and hence more Cl, is got than afterwards. In practice, only the gases from the decomposing pots, say 68–70 p.c. of the total HCl, are used for the Deacon process, those coming from the roasters being too dilute and containing too much sulphuric acid. In order to equalise the operation to a certain extent, the gases from two salt-cake pots can be mixed and the pots worked alternately, so that the strong gas from the early part of one charge is mixed with the weak gas from the latter part of the other charge.

The quantity of air necessary to form chlorine enters through the joints of the doors and dampers. It is regulated by the speed of the aspirator (a Root's blower) or cast-iron fan, which is placed at the end of the whole apparatus and produces the movement of the gases through it. Usually there are 4 vols. of air to 1 vol. of HCl. An excess of air is less injurious than a deficiency of it, in which case there is a poor decomposition.

The gases leaving the pot are first cooled by a long string of pipes and a scrubber; thus much of the water and about ⅓ or ½ of the HCl is removed. A patent by Deacon and Hurter (Eng. Pat. 2104, 1888) provides for cooling the gas and drying it in a sulphuric-acid tower before it enters the decomposer, such complete drying being very advantageous for the process. The gases now enter the heating apparatus. This is a furnace, 16 feet × 16 feet, in which twenty-six vertical pipes, 12 inches wide and 9 feet high, are arranged in two sets of twelve each, connected like the 'breeches pipes' in the blast-heating stoves, formerly used in iron works and now replaced by brick heaters.

The gases are here heated up to 500°; the waste heat of the furnace is sufficient for heating the decomposer, which does not possess any fire of its own.

The gases now pass into the decomposer (Fig. 8). This is an upright cast-iron cylinder, 12 to 15 feet wide. It contains a cylindrical ring of broken bricks supported by cast-iron shutters. The gases enter at the circumference at A, pass radially across the decomposing mass D into the inner space, and are led away through the pipe OB. The annular space between the shutters is 3 feet wide, and is divided into six compartments, one of which is emptied every fortnight. This is done by means of the discharging doors C, C below the cylinders. Fresh decomposing material is then thrown in from above through E, E; this material consists of burnt clay broken up into lumps, or ordinary bricks broken, freed from dust, and dipped into a solution of cupric chloride. The mass contains about 0·6–0·7 p.c. of metallic copper. After the active substance has served once, that is, for 10 to 12 weeks, it is thrown away. Each cwt. of clay produces about 10 to 12 cwts. of bleach. It has been found useless to attempt utilising the contact substance by redipping it in the copper solution or in any other way. The cost of copper for the contact substance does not exceed 1*s.* per ton of bleach produced.

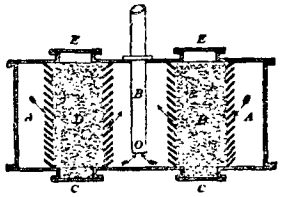


FIG. 8.

The temperature, both in the heating apparatus and in the decomposer, must be most carefully regulated, for which purpose special pyrometers have been constructed (*cf.* Hurter on Pyrometers, J. Soc. Chem. Ind. 1886, 625). In the decomposer, it ought to range from 480° to 500°.

When the gases leave the decomposer, they consist of a mixture of HCl, free Cl, and steam. In the best case, two-thirds of the HCl is converted into chlorine, but sometimes only one half. They are now cooled by passing through a long string of earthenware or glass pipes, and are then freed from HCl by washing with water in the ordinary acid condensers, consisting of stone coke towers, combined or not combined with acid cisterns, Woulff's jars, &c. By properly managing this process, all the acid can be obtained in the strong state, as required for the Weldon process and other purposes.

The gases can now be employed directly for making bleach liquor or chlorate liquor from

milk of lime. If, however, bleaching powder is to be made, they must be freed from water by passing them through a lead tower packed with coke, in which sulphuric acid of not less than 140°Tw. is kept trickling down. The removal of water is very necessary for dealing with this gas, which, owing to the great excess of nitrogen and oxygen present, contains at most 10 p.c. of chlorine, and cannot be absorbed in ordinary bleaching-powder boxes, but must be treated in apparatus specially constructed for this purpose (*cf. infra*). As will be seen from the description, there is theoretically no loss of HCl in the Deacon process, the whole of the acid evolved from the salt being either converted into chlorine or recovered by condensation as liquid hydrochloric acid. In practice, of course, some losses occur, but they are not necessarily large, and their amount depends principally on the efficiency of the draughting arrangements and the avoidance of low-level escapes at the salt-cake pots and furnaces. The fuel used per ton of bleaching powder to heat the decomposing apparatus depends naturally on the efficiency of working of the process, and varies from 6 to 10 cwts. per ton of bleaching powder.

During the early years of its existence, the Deacon process had many difficulties to contend with, and the working results were disappointing and unsatisfactory.

The fact that the impurities accompanying the gaseous HCl were sufficient to seriously affect the process was not realised. The impurities are sulphuric and sulphurous acid, arsenious acid, water, and carbon dioxide.

The sulphuric acid and sulphurous acid carried along with the gaseous HCl, especially when attempts were made as they frequently were in the early days, to utilise the roaster or furnace gas as well as the pot gas, converted the $CuCl_2$ into $CuSO_4$, which requires a higher temperature and gives a lower decomposition than $CuCl_2$.

The arsenious acid derived from the As_4O_6 in the sulphuric acid used forms arsenate of copper, which is even less reactive than the $CuSO_4$. The presence of these impurities necessitated the frequent renewal of the decomposing material. Water is one of the products of the decomposition, and hence, when present in the inlet gases, increases the partial pressure of the products of the reaction and lowers the maximum p.c. decomposition obtainable under the conditions of the process.

Carbonic acid derived from the fuel gases, either of the salt-cake furnaces or of the decomposing furnace itself, was a serious obstacle to, and frequently entirely prevented, the production of strong bleaching powder. This difficulty has been overcome by greater care in the construction of the apparatus and testing for leakage.

It will be noted from the above description that only the gaseous HCl from the salt-cake pot is dealt with by the Deacon process, and that allowing for the liquid acid collected after the decomposers, about 60 p.c. of the total acid is obtained in the liquid form, and has to be sold as such or used in some other way such as by the Weldon process.

Hasenclever, however (Eng. Pat. 3393, 1883), describes a process for gasifying the HCl in the liquid acid by mixing with strong hot sulphuric acid in a series of earthenware vessels through which air is blown.

By this means, a steady continuous stream of gaseous HCl is evolved with an easily regulated supply of air.

After passing through the series of vessels, the vitriol diluted with the water contained in the liquid hydrochloric acid has to be reconcentrated to the original sp.gr. The concentration is generally performed in long, lead brick-lined pans, heated by top heat, the fuel gases being in direct contact with the sulphuric acid. This process is used to a considerable extent, but from the large quantity of sulphuric acid to be concentrated per ton of bleaching powder, a very material addition is made to the cost of manufacture.

Chlorine produced from hydrochloric acid and air by other contact substances. Many such substances have been the objects of proposals, some of which are inseparable from the manufacture of chlorine from metallic chlorides, that is, from HCl in the nascent state. A general investigation on the mutual action of HCl and O in the presence of certain metallic compounds (of Cu, Fe, Mn, and Cr) has been made by Lamy (Bull. Soc. chim. 1873, 20, 2). We must refer to the original, and will only mention that copper salts were found to be much more efficient than others, and that with these the decomposition is at its maximum at about 440°.

The proposals to employ ferric chloride (Thibierge, 1855, and others) or chromic oxide (Hargreaves and Robinson, 1872) have not had any practical success.

Nickel oxide has been proposed by L. Mond (Eng. Pat. 8308, 1886). He passes HCl over heated NiO, when the chlorine combines with the base. The product is then in the same apparatus exposed to dried and heated air, whereby NiO is reformed and Cl is given off. In order to increase the active surface, pumice stone is impregnated with the chloride, and after drying the mass is exposed to the action of the gases in cylinders made of earthenware or enamelled iron. The gaseous HCl and air being previously heated, the retorts do not require very much additional heat from without, and therefore can be made of a large diameter. It is claimed for this process that it converts the HCl completely into chlorine, and that impure HCl, which is unfit for the Deacon process, is here quite suitable.

De Wilde and Reychler proposed (Eng. Pat. 17272 and 17659, 1889) to employ a mixture of magnesium and manganese chlorides with magnesium sulphate. The reaction takes place in two stages.

(1) $Mn_3O_8Mg_3+16HCl = 3MgCl_2+3MnCl_2+8H_2O+4Cl.$

(2) $3MgCl_2+3MnCl_2+8O=Mn_3O_8Mg_3+12Cl.$

The process is not, as far as is known, actually worked.

Chlorine from the residual liquors of the Ammonia-Soda process. The principal, at present the only, reason why the ammonia-soda process has not superseded the Leblanc process, is the fact that the chlorine of NaCl in the former

process goes to waste in the form of $CaCl_2$. Very numerous processes have been proposed and tried to avoid this loss by preparing HCl or free Cl from the liquors of the ammonia-soda process.

None of the processes proposed is, as far as is known, being worked or appears likely to be worked: we therefore confine ourselves to giving a list of the leading patents taken out.

1. *Chlorine from ammonium chloride.*—The most persistent efforts for the direct manufacture of chlorine from NH_4Cl were made by Mond, who took out the English patents: Nos. 65, 66, 1049, 3238, 8308, of 1886; 10955 and 17273 of 1887; 2160 and 2575 of 1889. Articles dealing with the Mond process are found in J. Soc. Chem. Ind. 1892, 466; 1893, 10; and 1893, 63.

There was also a proposition from the Verein Chemische Fabriken of Mainz (Eng. Pat. 3322 of 1886).

2. *Chlorine from* $CaCl_2$.—Persistent efforts for the direct recovery of the chlorine in the $CaCl_2$ produced in the ammonia stills of the ammonia-soda process were made by Solvay: Patents 77 and 171 of 1877; 838 of 1880; 7258 and 7259 of 1884; 8724 of 1885; 13389 of 1886; 18574 of 1888. Other patents: Twynam's process (Eng. Pat. 731 of 1885); Bramley's process (Eng. Pat. 8289 of 1887); Lyte and Steinhart (Eng. Pat. 21225 of 1890).

Chlorine from magnesium chloride.—Many efforts were made by Weldon to produce chlorine direct from $MgCl_2$; his patents are: Eng. Pt. 565 of 1868; 967, 968, of 1881; Weldon and Péchiney, 9305, 11035, of 1884; 14653, 14654, of 1887.

Detailed description of the Weldon-Péchiney experimental plant at Salindre, is given by Dewar (J. Soc. Chem. Ind. 1887, 775).

Other patents are: Wilson (Eng. Pat. 3098 of 1885); Gamble (Eng. Pat. 11581 of 1888); Lyte and Tatters (Eng. Pat. 17217 of 1889); Schlösing (Eng. Pat. 11821 of 1887; 11469, 11470 of 1891). (*See also* Eschellmann, J. Soc. Chem. Ind. 1889, 2; comp. *ibid.* 100.)

Chlorine produced by passing HCl *gas over heated peroxide of iron or manganese* is the subject of a patent by H. Burns (No. 15448 of 1886).

Chlorine by permanganates has been the object of patents by Tilghman (1847), Condy (1866), Tessié du Motay (1871 and 1873).

Chlorine from chromates and HCl has been proposed by MacDougal and Rawson (1848), Peligot (Ann. Chim. Phys. [2] 411, 267), Gentele (1861), Shanks (1858), Claus (1867), Aubertin (1873).

Chlorine by heating metallic chlorides with MnO_2 *and* H_2SO_4 was patented by Binks in 1853.

Chlorine by the assistance of nitric acid or nitrates.—Baggs and Simpson (1864) proposed making chlorine from *aqua regia*. Dunlop (1847) patented the preparation of chlorine along with nitrous acid, by heating together common salt, sodium nitrate, and sulphuric acid; the nitrous acid is absorbed by vitriol and the chlorine is passed on to bleaching-powder chambers. This process was working for many years at St. Rollox; it was patented again by Roberts and Dale in 1868; and a patent running on similar lines is that of J. Taylor (No. 13025 of 1884).

Other processes employing nitrates or nitric acid, which have not had any practical success, are those of Banks (1839), Tessié du Motay (Bull. Soc. chim. 22, 48), Schlösing (Compt. rend. 55, 284). The later patents are those of Donald, Eng. Pat. 62 of 1887; and Just, Eng. Pat. 14857 and 14859 of 1888; Davis, Eng. Pat. 6416, 6698, and 6831 of 1890; Wallis, Eng. Pat. 13822 of 1892; and Krause, Eng. Pat. 16227 of 1894.

None of these processes was apparently a technical success, and as far as is known, none of them is worked.

The electrolysis of metallic chlorides. Recent years have seen a large development of electrolytic processes for the decomposition of metallic chlorides, chiefly those of sodium and potassium into chlorine and alkali. It was observed as early as 1800 by Cruikshank that on electrolysing a solution of common salt, caustic soda was formed at the negative pole. Berzelius, Hisinger, and Davy all worked on the same subject, but a long time elapsed before their observations were utilised in actual manufacture.

The difficulties experienced in the electrolytic decomposition of alkaline chlorides on a manufacturing scale have been first the cost of the electric current, and secondly the difficulty of preventing recombination of the chlorine liberated at the positive electrode or anode with the caustic alkali produced round the negative electrode or cathode.

The various electrical processes suggested or tried for the decomposition of alkaline chlorides are all attempts to overcome economically this difficulty of the recombination of the products of electrolysis.

Theoretically a current of 1 ampere liberates in 1 hour 1·3236 grams of chlorine.

The number of patents taken out since the year 1885 in connection with electrolytic cells for the production of chlorine, is enormous, embodying every variety of shape, design, and method of work. We shall only deal with a few representative samples, illustrating the broad classes of design which have, up to the present, been used industrially on a large scale.

The cells may be roughly divided into four classes.

I. The cells in which the electrolyte consists of the fused salt.

II. The cells in which the electrolyte is a salt solution, and in which the cathode and anode are separated by a porous partition or diaphragm.

III. The cells in which the electrolyte is a salt solution, but in which a moving mercury cathode is used to remove the sodium produced from the action of the chlorine.

IV. The cells in which the electrolyte is a salt solution, and which depend on sp.gr. to keep apart the alkali and chlorine produced.

Class I. *The Cell with the Fused Electrolyte.*—The best known examples of this cell are the Vautin and the Acker cell.

The Vautin cell (Eng. Pat. 13568 of 1893 and

9878 of 1894) electrolysed fused NaCl or KCl, with or without the addition of fluorides or other chlorides to lower the point of fusion, over a cathode of molten lead or tin with which the sodium or potassium formed an alloy. (*See* paper by Vautin, J. Soc. Chem. Ind. 1894, 448.)

The Acker cell is designed on the same principle as the Vautin cell and makes use of the lead cathode (*see* Eng. Pat. 6636 and 6637 of 1898).

Below is a sketch (Fig. 9) of the Acker cell,

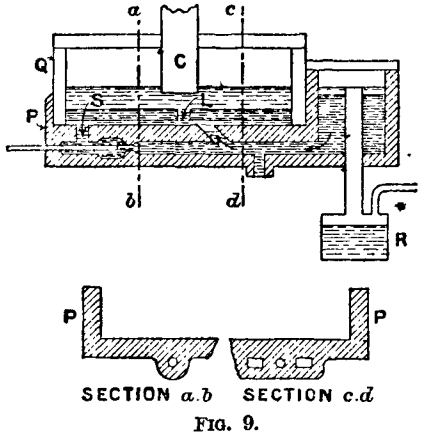


FIG. 9.

taken from a paper by J. B. Kershaw in Electrician, Oct. 25, 1901.

The bottom of the cell P is trough-shaped and of cast iron. It serves as electrical connection between the main conductor and the mass of fused lead L resting on it. The upper part of the cell Q is constructed of any refractory basic material not attacked by chlorine gas or fused salt. The anode C is of carbon and dips into the fused salt.

The channels and subsidiary vessel R are arrangements designed to remove and decompose the lead alloy as it becomes sufficiently saturated with sodium. The decomposition of the alloy is effected by blowing steam into it, and the heat generated by the conversion of the sodium into hydroxide is returned to the cell and assists in maintaining the necessary temperature.

The voltage actually taken by the Acker cell is 6·75, and the current efficiency 54 p.c. (Report of Commission on Science and Arts, J. Franklin Inst. 1903, 156).

The Acker cell was worked at Niagara Falls on an industrial scale, from about 1900 to 1907, when the works were completely burned down and have not been rebuilt.

Class II. *The Porous Diaphragm Cells.*—The best known of the diaphragm cells is the Griesheim cell, which has been used on a very large scale for some years in Germany, and also in Spain, France, and Russia.

Figs. 10, 11, and 12 represent the Griesheim cell. A is the anode cell; K, the cathode cell; C, the carbon anodes; M, a steam-jacket; Z, the salt charging pipe; L, the chlorine exit pipe; B, sheet-iron plates acting as cathodes.

Six to twelve cells are usually worked in series. Each cell contains one or more anodes which are fastened to the cover. The bath which forms

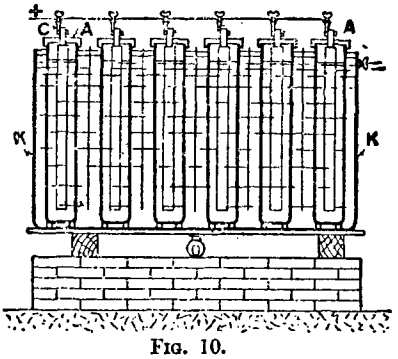


FIG. 10.

the cathode compartment is provided with a gauge glass and a run-off tap for the caustic lye formed, while the hydrogen evolved passes away by a pipe to a gas holder.

The porous diaphragm invented by Breuer

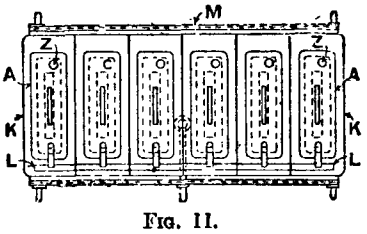


FIG. 11.

(D. R. P. 30222 of 1884) is made by mixing cement, common salt, and hydrochloric acid into a paste and casting into any shaped articles required. The porous diaphragms which form the wall of the anode compartment are set in iron frames like windows, and are cemented in. The whole interior surface of the cell is also covered with cement.

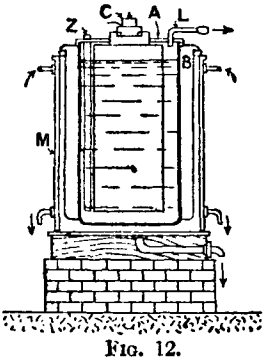


FIG. 12.

A great improvement was made in this cell by the substitution, for the carbon anodes, of anodes made of iron oxide, produced by melting Fe_2O_3 in the electric arc and casting the Fe_3O_4 produced into plates. The advantages of the iron-oxide anodes are that first the formation of CO_2 from the oxidation of a carbon anode is avoided, and chlorine free from CO_2 is produced; and secondly, that the oxygen, which with the carbon anode forms CO_2 with the oxide of iron anode, forms the alkaline chlorate, which can be recovered as a valuable by-product. (For further information, *see* paper by Lepsius,

Ber. 1909, 2892, from which the above is abstracted.)

The Hargreaves-Bird Cell.—The following illustration shows the Hargreaves-Bird cell (Eng. Pat. 18871 of 1892; 5197 and 18173 of 1893).

The peculiarity of this cell is that the porous diaphragm and cathode are in one, and are made in the following way.

A layer of porous material, such as asbestos in the form of pulp, is plastered on to one side of a sheet of iron netting. On to the outside of the fibrous material is then deposited a layer of Portland cement. In some cases the fibrous material is omitted. The wire netting acts as cathode.

As is shown in Fig. 13, the cell consists of an

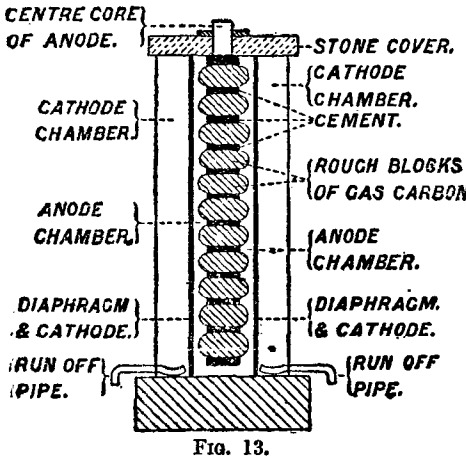


FIG. 13.

outer trough in which is placed the inner vessel, formed by the porous diaphragm. The cathode or the wire netting is, of course, on the outside.

The inner or anode compartment is filled with brine; the outer cathode compartment is empty, but the wire gauze is continually washed with either steam or a water spray to remove the alkali as it is formed. The cell is usually worked with an atmosphere of CO_2 in the cathode compartment, and thus produces chlorine and carbonate of soda. When attempts are made to produce caustic soda by this cell, the current efficiency falls most seriously through conduction of current by the NaOH on the cathode.

A paper on this cell, by Hargreaves (J. Soc. Chem. Ind. 1895), states the current density as 18·7 amperes per square foot; the E.M.F. as 3·4 volts per cell; the current efficiency as 80·3 p.c. The present working is understood to give a current efficiency of about 90 p.c., and to require 4 volts per cell.

The Townsend cell (Eng. Pat. 18403 of 1904) resembles the Hargreaves-Bird cell with this difference, that the cathode compartment is filled with kerosene oil which washes the alkali as it is formed off the cathode, and thus makes it possible to produce chlorine and caustic soda in this type of cell without great loss of current efficiency. Kershaw (Electrician, April 24, 1908) gives the current efficiency as 90 p.c., and the voltage per cell as 4·7.

The Finley cell (Eng. Pat. 1716 of 1906) is a remarkable cell, in that it has a double diaphragm dividing the anode and cathode compartments. The diaphragm is very open in texture, and the brine feed for the cell is run into the centre compartment between the two diaphragms, from where it passes outwards on either side to the anode and cathode compartments. In this way, an additional obstacle, depending for its strength on the speed of feed of the brine, is interposed to prevent intermixture of the products of the electrolysis.

Class III. The cells which depend for the separation of the soda from the chlorine on *a moving cathode of mercury.*

The mercury cathode for the preparation of alkali metals was first used by Davy; it was described in an application for a patent (Eng. Pat. 4349 of 1882) by Nolf. It is mentioned again in Hermite's patent, 3957 of 1886. Further patents describing its use are Hermite and Dubose, Eng. Pat. 21959 of 1891; Greenwood, Eng. Pat. 5999 of 1891.

The general principle of these cells is that the electrolysis takes place between an anode above and a cathode of mercury vertically below. The chlorine liberated naturally rises upwards and out of the solution, and the sodium or potassium freed combines with the mercury to form an amalgam. The amalgam, when sufficiently highly saturated with the alkaline metal, is replaced by fresh mercury and the amalgam itself decomposed by water, with the liberation of H and the formation of a caustic alkaline solution.

The various patents taken out and cells suggested differ chiefly in the method adopted for the movement of the mercury.

To Castner, however, belongs the chief credit of making the mercury cell technically successful. Castner (Eng. Pat. No. 16046 of 1892) employs a moving mass of mercury, connecting up the anode and cathode chamber. Patent No. 10584 of 1893 makes this process continuous by moving the mercury by a rocking motion of the cell, *see* Fig. 14, which represents the original rocking cell.

Castner also claims sodium amalgam as

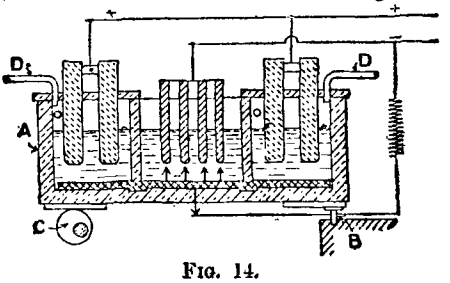


FIG. 14.

alternate anode and cathode, the utilisation of electric energy produced by decomposition of the amalgam and the passing of different quantities of current through the NaCl and NaOH.

A is the cell itself divided into three compartments, the back end being adjustable by the knife edges B. The front end of the cell rests on an eccentric, C, revolving on a shaft; this gives the rocking motion. The two outer or anode compartments have carbon anodes and are filled with saturated brine; the centre compartment contains iron cathodes and is filled with

NaOH solution. A layer of mercury, about ¼ inch thick, lies on the bottom of the cell and alternately flows from first one and then the other anode compartment into the cathode compartment. The chlorine liberated in the anode compartment is carried away by pipe D.

Castner, in the Chemical Trade Journal, 1894, 211, stated that the results of 1 week's work on a unit of 28 working cells, arranged in two parallel series of 14, gave a yield of 930 lbs. chlorine and 1120 lbs. NaOH per 24 hours; the amperes used averaging 571, and the volts 5·1 or 3·9 per cell.

More recent mercury cells are the

1. *Kellner pressure-displacement cell*, which differs from the Castner in the point that the

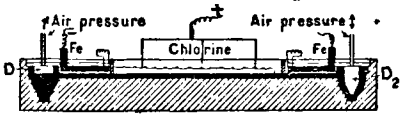


FIG. 15.

chlorine compartment is placed in the centre of the cell surrounded by the caustic compartment, which is provided on either side with a recess, DD, which forms the alternative receptacle for the mercury. The mercury is forced to move continuously from side to side by compressed air.

Above (Fig. 15) is a sketch which shows the construction and working of the cell, taken from the Chemiker Zeitung, Oct. 30, 1909.

The anodes are platinum gauze, and are placed in a cement box which has proved more satisfactory than the stoneware jars formerly used.

The anodes, including the platinum fastener, weigh 1 gram apiece. Each cell contains six electrode boxes, and each box holds 88 pieces of platinum gauze, 2×2 inches square, weighing in all about 525 grams. The cathodes are cast iron, cast in grill shape. The current used is 4000 amperes per cell.

The great advantage of this cell is the high-current density which has resulted in considerable reduction of plant.

2. *The Kellner-Solvay Scoop Wheel Cell.*—This cell consists of two slanting troughs communicating with one another, in which the mercury is kept in constant circulation by a rotating scooped wheel. This cell is built in very large units, taking up to 10,000 amperes, and it is

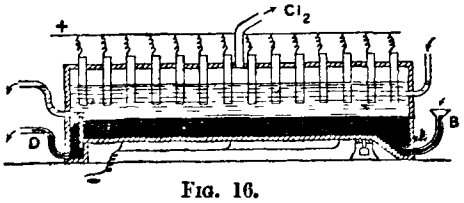


FIG. 16.

said that a 15,000-ampere cell is well within the bounds of possibility.

Fig. 16 is a sketch of the Kellner-Solvay cell, B being the mercury inlet and D the outlet for the amalgam; the scooped wheel is, however, not shown.

Another cell depending for the mercury circulation on a revolving scooped wheel is the Whiting cell, shown in Fig. 17.

3. *The new Castner-Kellner cell* differs from the Kellner-Solvay cell in the method of conveyance of the mercury, which, in this case, is effected by means of an Archimedian screw. Taussig, before the International Congress of Applied Chemistry, 1909, states that carbon anodes have been abandoned and anodes of platinum gauze substituted.

The current efficiency of the modern mercury cell is stated to be not less than 90 p.c., and the voltage required 4·3 volts.

Professor Lepsius (Ber., *loc. cit.*) enumerates the following advantages and disadvantages of the mercury cell as compared with the diaphragm cell:—

The advantages of the mercury cell are: (1) the purity of the caustic alkali produced, which is a very important advantage; (2) the comparatively high concentration of the caustic solution; (3) the high current efficiency and absence of evolution of oxygen.

The disadvantages of the mercury cell are:—

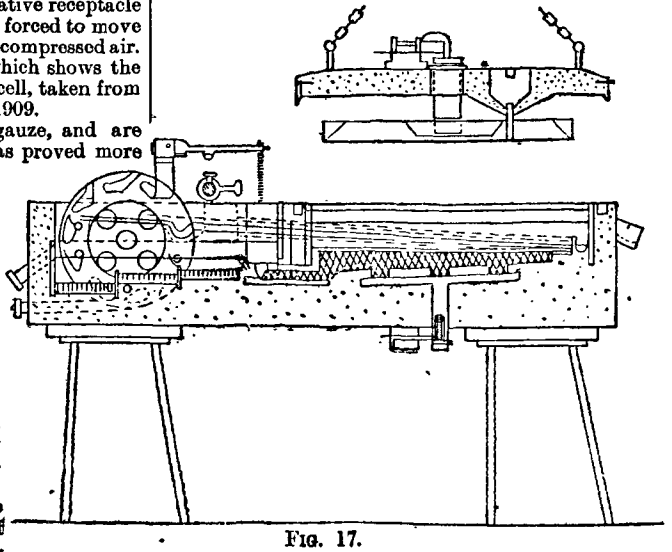


FIG. 17.

(1) the higher voltage, 4·3 volts as against 3·5 volts in the diaphragm cell; (2) the cost of the mercury, of which 72 tons are required for a plant utilising 6000 h.p.; (3) the greater cost of installation apart from the question of the mercury.

IV. *The Specific Gravity Cell.*—The best known cell of this type is the so-called 'Glocken Cell,' patented by the Oesterreichischer Verein für Chemische und Metallurgische Produckte, and working on a large scale at Aussig, Berlin, and Stassfurt.

Fig. 18 shows the original type of the 'Glocken' or Bell cell, in which A is the anode and K the cathode, separated by the non-conducting bell D, E. The bath W is filled with salt solution, which enters at L and overflows at F. The chlorine escapes at C. Figs. 19, 20, 21 show the improved cell actually in use.

Owing to the fact that, when working, the

liquor round the anode is of lower sp.gr. than that round the cathode, at the bottom of the cell, little intermixture occurs, and owing to the

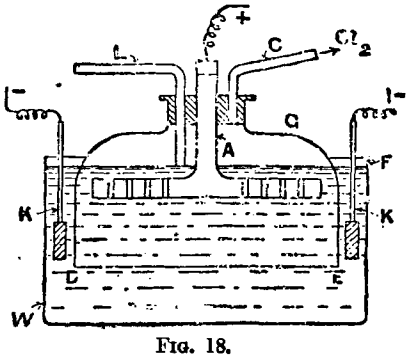


FIG. 18.

feed of fresh brine at L, a constant slow movement of the electrolyte downwards takes place.

The disadvantage of this cell, according to Lepsius, is its small size; for instance, at Aussig, 3000 h.p. are utilised and 25,000 cells required.

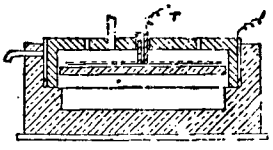


FIG. 19.

The voltage required lies between the Griesheim and the mercury cell, viz. 4 volts.

(For further detail, *see* Lepsius, Ber. *loc. cit.*, from which paper the above is largely abstracted.)

Liquid Chlorine.—Chlorine gas can be condensed to a liquid at atmospheric pressure at −34°, or at atmospheric temperature (15°) by a pressure of six atmospheres. Vautin (Eng. Pat. 8820 of 1887), Heinzerling (D. R. P. 49280),

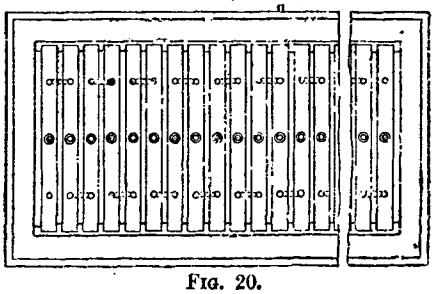


FIG. 20.

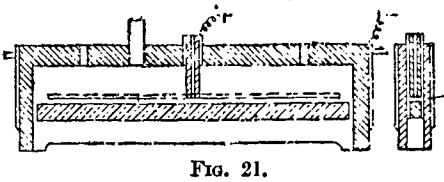


FIG. 21.

Hannay (D R. P. 49742) describe suggestions for manufacture of liquid chlorine.

The pioneers in the manufacture have been, however, the Badische Anilin und Soda Fabrik, who (Eng. Pat. 13070 of 1888) describe two apparatus (Figs. 22 and 23) for the compression of chlorine.

In Fig. 22, A, B is a U-tube of which the limb B and the lower part of A are filled with strong sulphuric acid. The upper part of A is filled with liquid paraffin, which floats on the acid. The limb B is first filled with chlorine by shutting valve C and opening valves D and E. When full, D and E are shut, C is opened, and the paraffin is forced into A by the pump. During

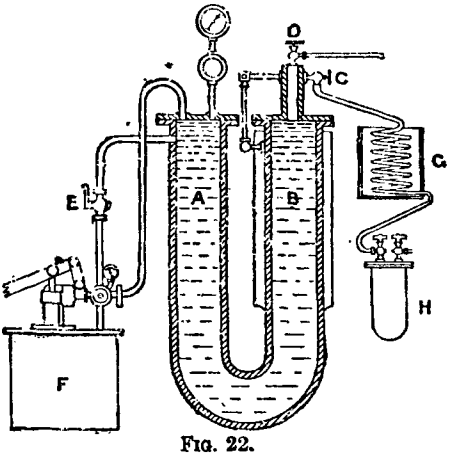


FIG. 22.

compression, limb B is heated by a water-bath to 50°–80°, in order to prevent liquefaction of the chlorine there.

The gaseous chlorine under pressure is forced through the cooling coil G, from which it runs as a liquid into the receiver H. The operation is then repeated.

Fig. 23 represents an apparatus working on the same principle as that of Fig. 22, but differing in detail.

The plunger A works in paraffin, with which the upper part of the vessel B is filled. The lower part of B and its continuation C and D are filled with strong vitriol, through which the pressure produced by the plunger A is transmitted to the cylinder D. The chlorine enters by F, and is condensed and collected after leaving the cylinder D, as in Fig. 22.

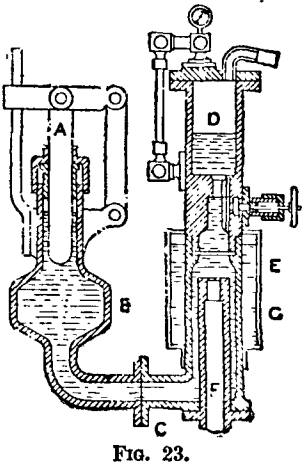


FIG. 23.

As in Fig. 22, the compressed chlorine has to be kept warm in the compression vessel, and this is done by the water-jacket G.

Marx (Eng. Pat. 7058 of 1890) proposes to make the liquid chlorine direct by the decomposition pressure of chlorine hydrate As far

as is known, this ingenious process has not been worked.

Chlorine, when dry, does not attack iron, and the liquid chlorine is safely carried and stored in iron and steel cylinders, tested to a pressure of 50 atmospheres.

Chloride of lime or bleaching powder. By far the greater part of the chlorine produced on a manufacturing scale is converted into *chloride of lime or bleaching powder.* Otherwise most of the hydrochloric acid produced in the process of decomposing common salt by sulphuric acid would be wasted; that portion of it which would be required by those preparing chlorine for bleaching purposes, &c., would cost any consumer not in the immediate neighbourhood of the works much more than the finished chloride of lime does now.

The first to suggest the industrial application of chlorine to bleaching was Berthollet, in 1785, and in 1789 was produced the liquor called 'Eau de Javel,' manufactured by passing chlorine into a solution of potash. This for the first time enabled the bleacher to buy his chlorine in an available form, but it was too dear for most purposes, and so was the kindred liquor made from soda. Both, especially the latter, have still some application in special cases, but their part is very small in comparison with that played by the analogous compound, manufactured with the cheapest of all bases, lime. The use of this was first suggested by Charles Tennant, in 1798, and this was all the more important as the alkalis were at that time enormously dearer than they are at present. At first Tennant used milk of lime, and thus obtained the solution known under the name of 'bleach liquor,' and extensively manufactured even now. In 1799 he took out his patent for absorbing chlorine by dry hydrate of lime, and the compound thus formed, 'bleaching powder,' was sold by the St. Rollox Works, established in the same year, at 140*l.* per ton.

Composition of Bleaching Powder.—The union of chlorine and lime seems to take place in a very direct way, and the composition and many of the properties of the new substance formed also seemed to favour the assumption that it was merely a compound of CaO and Cl_2; the name 'chloride of lime' was given to it on this assumption. Long before our present theories made it unlikely that CaO could combine as such with chlorine, Balard, in 1835, propounded the theory that bleaching powder was a compound or mixture of equivalent proportions of calcium hypochlorite and chloride

$$Ca(OCl)_2 + CaCl_2,$$

mixed with an excess of calcium hydroxide.

This theory, supported by Gay-Lussac in 1842, in point of fact explains nearly all the properties of bleaching powder. A more recent formula to represent bleaching powder, $Ca\begin{smallmatrix}Cl\\OCl\end{smallmatrix}$ was suggested by Odling, and by Lunge, Schäppi and Naef, who showed that $CaCl_2$ as such does not form part of dry bleaching powder, but is only formed on solution in water, and also that the excess of lime always found can be reduced to so small a quantity that none of the theories formerly advanced in order to explain the constant presence of such excess of lime can be upheld.

All these formulæ, however, leave out of account the water of hydration present in the lime before chlorination, which is not expelled, and which is absolutely necessary for the formation of the bleaching powder.

Preparation of Lime for Bleaching Powder.—The lime required for the manufacture of bleaching powder must be from as pure a limestone as possible and must be well burned. Among the most suitable limes for bleaching powder is that used in Lancashire, and made by burning the Derbyshire limestone in the district round Buxton. The average composition of this limestone is:

$CaCO_3$	98·9
$MgCO_3$	0·29
Fe_2O_3	0·17
Insol. etc.	0·35
H_2O	0·05
	99·76

The burnt lime is slaked by spreading it on a brick floor, sprinkling it with water and turning it over with a spade till it has completely fallen to powder, after which it is allowed to remain in a heap for 10 hours.

The slaked lime is then passed through a wire sieve of 12–18 wires to the lineal inch.

Mechanical lime-slaking apparatus is largely used, in which the burnt lime is treated with water in a closed vessel with continuous agitation. The mechanical apparatus has the advantage of producing a very uniform product in a much shorter time with less labour and a comparative absence of dust, which with the hand slaking is very trying to the workers.

The slaked lime as used for bleaching-powder manufacture contains about 25 p.c. H_2O, and should not contain more than 2·5 p.c. $CaCO_3$.

The Bleaching-powder Chambers.—The apparatus in which the chlorine is brought into contact with the slaked lime varies with the concentration of the chlorine gas to be treated.

With highly concentrated chlorine gas, such as that obtained from the Weldon stills, where the gases contain 85–90 p.c. Cl, simple chambers or boxes of large size are used, on the floor of which is spread a layer of lime.

The chambers or 'boxes' were formerly often made of tarred wood, masonry, or stone flags. For the ordinary strong chlorine gas, these have been in England universally replaced by large chambers of about 6½ feet in height, so that a man can work inside them, of a width of from 10 to 20 feet and more, and up to 100 feet long. Their sides and top are usually made of about 5- or 6-lb. sheet lead, fastened by straps on a timber framework, exactly like vitriol chambers.

The floor is made of large stone flags, or of coal-tar asphalt, the joint between the sides and the edge of the floor being specially protected by a skirting and asphalt poured behind it.

The chambers must be fitted with doors (generally made of iron protected by paint), with glass panes in two opposite doors for observing the colour of the gas, with 'lutes' for introducing the gas, and with some contrivance for removing the gas remaining at the end of the operation (*v. infra*).

Sometimes the chambers are not erected on the ground-level, but upon pillars, like vitriol chambers, leaving about 10 feet of clear space from the ground. In this case the packing of the finished bleach into casks can be done by means of trap-doors in the chamber floor, with wooden hoppers attached underneath, below which the casks are placed, the bleach being pushed down into them from above by means of wooden rakes.

Sometimes several chambers are combined to form sets, so that the gas always enters first into a nearly finished chamber, and the excess gas into a freshly charged chamber, where it is entirely taken up.

Jahne (Dingl. poly. J. 283, 287; J. Soc. Chem. Ind. 1887, 367) gives a number of observations made with a set of four chambers connected in this way.

Many proposals have been made for mechanical absorbing apparatus for strong chlorine, but none of them seems to have met with permanent success; sometimes the working parts are worn out after a short time, and sometimes the bleach produced in them is too weak. Of course, it cannot be said that the construction of a mechanical chlorine absorber for dry lime is an impossibility, but it must be difficult to construct unless a perfectly regular stream of chlorine gas is at command, and efficient means are employed for artificially removing the heat given off during the absorption.

The manufacture of the bleaching powder in the chambers takes place in this way. The hydrated lime is spread upon the floor in a layer of 4 to 6 inches in depth; its surface is drilled into furrows by means of a wooden tooth-rake, to assist absorption. All joints are plastered up with lime putty, and the gas is admitted, leaving at first an airhole open, which is only closed when chlorine issues from it. The gas is at first very quickly absorbed, as may be seen by its colour when looking through the glass panes, afterwards much more slowly. If there is not sufficient care taken to keep it free from acid and moisture, lumps are formed which are very injurious.

When the lime will not absorb the chlorine as fast as it enters the chamber, this is left to itself for 12 hours, or, better still, for 24 hours, after which time the chlorine will nearly always have been absorbed.

It is difficult to get full-strength bleach by one operation; there is always a superficial crust which prevents the gas from penetrating right through. It is, therefore, necessary to turn the stuff over with spades, and treat again with chlorine. Sometimes this must be done even a third time, before the appearance of the product, and the laboratory test show it to be finished. It ought then to consist of pretty heavy flakes, easily crushed, but not dusty, which can be kneaded with the fingers into a tough paste. The laboratory test of a sample carefully taken from various parts of the chamber ought to be at least 37 p.c. available chlorine. With impure, badly burnt, badly slaked, or badly sifted lime, with moist chlorine or such as contains carbon dioxide, no strong bleach can be expected, and when trying to force this by 'gassing' too much, it will be found that the strength actually goes back, calcium chlorate and chloride being formed.

As it is indispensable to employ an excess of chlorine in order to finish the bleach, there must be always a great quantity of unabsorbed gas in the chamber at the end, and if no special precautions are taken in this respect, the opening of the doors will cause an intolerable nuisance. This ought to be prevented in any case. It can be done by drawing the gas out of the chamber, either by chimney draught or by mechanical means, and making it to pass through a milk-of-lime or even through a hydrate-of-lime absorber.

Probably the best means for this end is the plan patented by Brock and Minton (Eng. Pat. 7199, 1886; comp. 23rd Report on Alkali, &c., Works, 58–60), who, before opening the door, sprinkle lime into it by means of a wooden hopper and fan fixed in the roof, in such quantity that the free chlorine is entirely absorbed without bringing down the strength of the chamber below the required point. There is thus also an additional yield of bleach. Lime in fine powder is put into the hopper fixed in the roof of the chamber, and is admitted into the latter by means of a valve. A vertical shaft, inside a box between the hopper and the valve, is made to turn by a handwheel, and, being armed with blades, forms a fan or distributor, which draws air from the chamber, mixes it with the descending lime, and causes this to pervade every part of the chamber. One such machine is sufficient for a chamber of 100 feet length, but generally three are provided. This treatment reduces the amount of chlorine in the chamber air to less than 1 grain per cubic foot (0·82 on the average), without materially reducing the strength of the bleach. For a chamber of 10 tons bleach, finished with a considerable excess of chlorine, 4–5 cwts. of lime dust are thrown in, which produce 6 cwts. of bleach. It requires an hour or two to settle, but the whole of the operation is complete in 3 hours. The doors can then be taken down without any strong smell being perceptible within a few feet of the chamber, and packing can at once be proceeded with. The extra bleach produced much more than pays for the treatment.

For testing the amount of chlorine in the air of bleaching-powder chambers previous to opening the doors, several kinds of apparatus have been proposed: *e.g.* that of Ballard (21st Report on Alkali, &c., Works, 37; 22nd do. 55) and of Stark (J. Soc. Chem. Ind. 1885, 311). Ballard's apparatus consists of a cylindrical glass jar, closed at the top by an indiarubber cork, through which the nozzle of a 4-oz. enema ball (finger pump) passes, as well as an elbow tube reaching down to the bottom. The lower end of this tube is closed at the lamp, so as to leave an opening fine enough for a needle only to pass through. The horizontal branch of this tube is inserted in the side of the chamber at a point about 2 feet from the bottom. When compressing the ball, the air is driven out by a small hole made in the nozzle just above the cork; this is now closed by the finger, and on relaxing the pressure the ball will expand, and will cause 4-oz. measures—that is, $\frac{1}{15}$ of a cubic foot—of chamber air to enter into the jar and bubble through the test solution contained therein. This is continued till the end of the reaction is indicated by the test liquor turning blue. The latter consists of 3·485 grains of

arsenious acid, dissolved in sodium carbonate and rendered neutral by sulphuric acid, to which is added 250 grains potassium iodide, 50 grains precipitated chalk, 10,000 grains water, 6–10 drops ammonia. For each test 400 grains are used, adding a little starch paste at the time of using. When 2½ grains of chlorine per cubic foot are present in the chamber air, ten aspirations of the chlorometer will cause a blue colour to appear; if more aspirations are needed, there is less chlorine present, and *vice versâ*. Stark's apparatus attains the same end, not by the finger pump (which is certainly a somewhat rough instrument), but by a gas burette on the Orsat principle.

The following rules are recommended by the Chief Inspector of Alkali, &c., Works (Mr. A. E. Fletcher), in his 21st Report, 12:—

I. Bleaching-powder chambers should contain not less than 200 square feet of floor space for every ton of powder made in them per week. If there is less space, the work, and especially the packing, must be hurried too much.

II. The chambers should be so arranged and connected together that the residual chlorine from a finished chamber may be drawn into one containing fresh lime, unless some other means be employed for absorbing it (such as Brock and Minton's plan described above). The air finally discharged into the atmosphere or into a flue or chimney must not contain more chlorine than 2½ grains per cubic foot.

III. No chamber should be opened when the air in it contains more than 2½ grains of chlorine per cubic foot. In testing for this, the air should be drawn from a point not more than 2 feet above the chamber floor, and taken from the draught end.

IV. No chamber may be opened until the air in it has been tested, and the result of such test entered in a book.

V. No chamber may be opened except in daylight.

The control of the temperature in the bleaching-powder chambers is very important, as the absorption of chlorine by hydrated lime to form strong bleaching powder takes place within comparatively narrow limits of temperature.

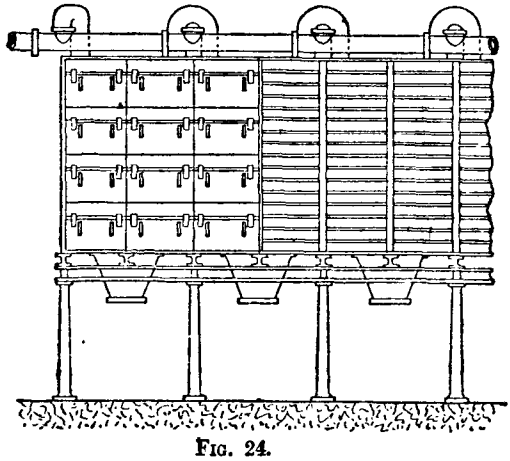


FIG. 24.

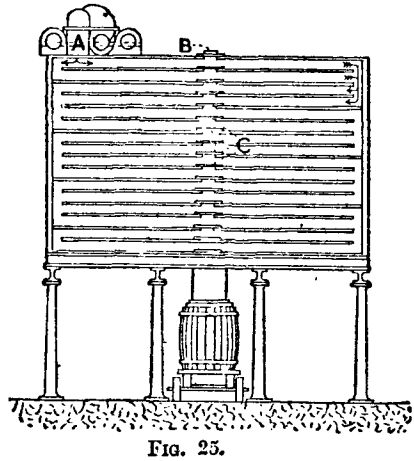


FIG. 25.

In the hot weather of an English summer difficulty is often experienced through overheating, and in cold winter weather, especially in chambers in an exposed situation, and when working slowly, the absorption is so slowed down that strong bleach cannot be made.

The absorption of weak chlorine, that is, chlorine diluted with very much nitrogen and oxygen, as it is obtained in the Deacon process, and in most of the processes proposed for dealing with calcium and magnesium chlorides, cannot be carried out in the ordinary chambers. The most efficient plant for this purpose seems to be that worked out by Deacon himself. The absorbing space is immensely increased, and at the same time the process is made a continuous operation by employing a large number of chambers, each of them provided with a number of shelves, and connecting them in such a way that the fresh chlorine gas always enters the chamber in which the bleach is nearly finished, and the last gas, then containing only traces of chlorine, is passed through a chamber just charged with fresh lime. These chambers cannot very well be made of any other material than of stone, slate, sandstone flags, volvic lava, &c. The distributing pipes are of cast iron. The chambers are arranged in pairs, the gas being made to pass down the one half and up the other half of the pair.

Practically a set of Deacon chambers consists of seven double chambers with sixteen shelves each, with a total area of 1250 square feet, upon which 18½ cwts. of calcium hydroxide can be laid ½ inch to 1 inch thick. Every 16 hours one of the pairs of chambers comes in turn to be drawn and recharged. Hurter has shown that such chambers would not be applicable to strong chlorine, as then the temperature would rise to 70° or 80°, but in the present case the inert gases, of which there are about 90 p.c. present, prevent the temperature rising to any hurtful extent.

Figs. 24 and 25 show a front elevation and a sectional elevation of these chambers.

The gas enters from pipe A into the top of the first chamber, and travels down over the shelves in it, as is shown by the arrows in Fig. 25. From the bottom of chamber 1 the gases pass into the bottom of chamber 2, thence upwards over the shelves as in chamber 1.

A block of such chambers containing 14 chambers, each with 16 shelves, will produce 25–30 tons of bleaching powder per week.

Before starting to lime the chambers, the cover B is removed, and the wooden slides C are pushed on one side, with the exception of that on the bottom shelf. Sufficient lime to cover one shelf with a layer nearly 1 inch thick is then dropped through the hole from which B has been removed, and falls down to the bottom shelf. There it is spread and then raked into furrows by rakes through the ends of the chamber from which the sheet-iron doors shown on Fig. 24 have been taken down. When this is done, the slide C on the bottom shelf but one is pushed over the hole and the lime charge for that shelf dropped and levelled as before. The rest of the shelves are then limed similarly one by one.

The finished bleaching powder is packed in a similar way by first pushing on one side the slides C, and then pushing the bleaching powder, made on the separate shelves, to the centre of the chamber, where it falls through the holes down to the cask below.

Hasenclever (Eng. Pat. 17012 of 1888) describes a mechanical chamber for the production of bleaching powder, which has been at work successfully with weak chlorine such as the Deacon chlorine, for many years.

Figs. 26 and 27 show the Hasenclever mechanical chamber, which consists of several superposed tubes, into the top one of which the lime is fed, and through the series of which it is caused to travel by the agitators, finally dropping into a hopper which delivers into the cask.

The chlorine gas travels in the opposite direction to the lime, and enters the bottom cylinder.

The *yield* of bleaching powder may be taken as 1½ times the weight of the calcium hydroxide.

Bleaching powder must be packed in very well-made casks, preferably made of hard wood.

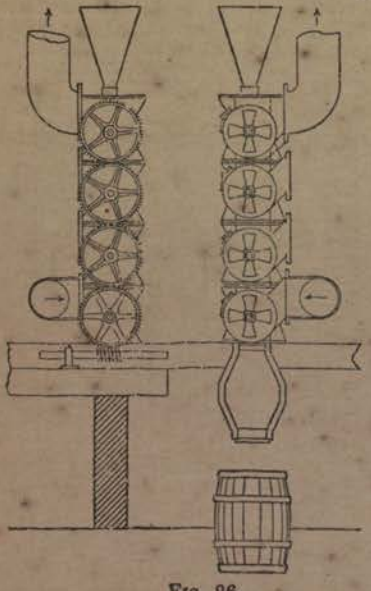


FIG. 26.

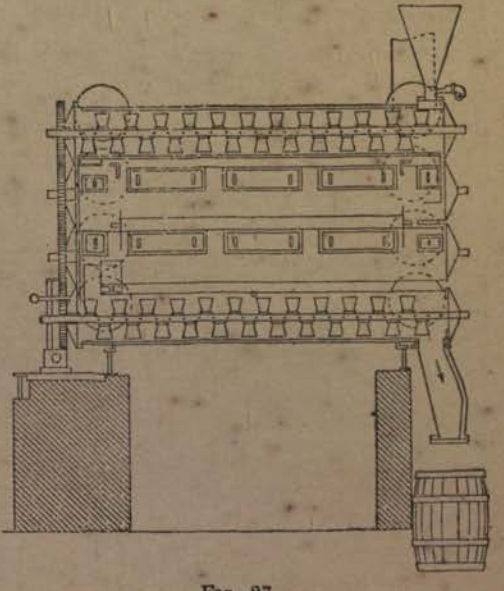


FIG. 27.

The ends are sometimes secured by a coat of plaster of Paris. This is done in order to prevent the access of air, which quickly deteriorates the powder both by its moisture and its carbonic acid.

The packages must be kept in cool, dry places; both rain and sun would quickly spoil the bleaching powder, even if packed in good casks.

Properties of Bleaching Powder. — Good bleaching powder is a pure white powder, often mixed with lumps which, however, ought to be transformed to the core, and which are often removed by riddling. It has a peculiar smell, quite different from that of chlorine, and not owing to hypochlorous acid, since it is just as perceptible in alkaline solutions, or on the skin after washing with soap, &c. It may possibly be due to the action of the compound upon organic matter.

In the air bleaching powder attracts moisture and carbonic acid, and gradually changes into a pasty mass. Mixed with a little water, it forms a stiff paste, with a perceptible swelling and rise of temperature; this is probably caused by the transformation of $2CaOCl_2$ into $Ca(OCl)_2$ and $CaCl_2$.

Bleaching powder decomposes gradually even in closely stoppered bottles or well-protected casks. The presence of light, heat, moisture, and carbonic acid greatly accelerates this change; so does shaking, *e.g.* in transit. Hence the strength of bleach is usually only guaranteed at the place of shipment, but it ought not to lose above 2 or at most 3 p.c. by a few weeks' journey.

Experiments on the rate at which bleaching powder loses its available chlorine have been made by J. Pattinson, in 1874 (Chem. News, 29, 143) and 1886 (J. Soc. Chem. Ind. 587). He experimented in the first case with samples kept in loosely corked bottles, sheltered from direct sunlight, and found that these lost on an

average 0·33 p.c. monthly from February to April, 0·86 from June to September, 0·28 from November to January. The greatest loss occurred in August, viz. 1·4 p.c. per month.

The keeping properties of bleaching powder depend on the quality of the lime used, on the temperature conditions under which it has been made, and on its strength. The more free calcium hydroxide is left in the bleaching powder, the more stable it is. This shows that, when bleaching powder is required for export, especially to tropical countries, it is a mistake to require a high initial test.

The experiments made by Lunge and Landolt (J. Soc. Dyers and Colorists, 1885, Nov. 25), with bleach liquor have also shown that the action of the air is nothing like so injurious to the stability of such solutions as that of the light, which ought to be excluded by all means. Solutions kept in the dark in closed vessels, remained practically unchanged up to the 24th day, and up to the 33rd day, when the experiment was finished, the strength had only decreased from 29·58 to 29·12. Kept in open vessels in the dark, they remained unaltered up to the 12th day; on the 33rd day they had lost 3·30. But when kept in closed vessels in diffused daylight, the decomposition set in at once, and on the 33rd day only 8·52 remained of 33·02 originally present. Solutions of chloride of magnesia behaved similarly to those of chloride of lime; those of zinc or aluminium hypochlorite, as might be expected, were much less stable.

A few experiments made by Thümmel (Arch. Pharm. 1834, 22, 1) also prove that light has much more action on bleaching powder than exposure to air.

The following complete analyses of the samples of bleaching powder investigated by J. Pattinson (*v. supra*) may serve as an example of the best descriptions of the commercial article: —

——	A made of Irish limestone (from Larne)	B made of Irish limestone by another manufacturer	C made of French cliff
Available chlorine	37·00	38·30	36·00
Chlorine as chloride	0·35	0·59	0·32
Chlorine as chlorate	0·25	0·08	0·26
Lime	44·49	43·34	44·66
Magnesia	0·40	0·31	0·43
Ferric oxide	0·05	0·04	0·02
Alumina	0·43	0·41	0·33
Oxide of manganese	trace	trace	trace
Carbonic acid	0·18	0·30	0·48
Silicious matter	0·40	0·30	0·50
Water and loss	16·45	16·33	17·00
	100·00	100·00	100·00
Total chlorine	37·60	38·97	36·58

The following are analyses of bleaching powder made by Lunge and Schäppi, from perfectly pure lime and with the greatest care, so as to obtain the strongest possible product:—

Available chlorine	43·13
Chlorine as chloride	0·29
Lime	39·89
CO_2	0·42
H_2O (direct estimation)	17·00
Calculated as:	
$CaOCl_2+H_2O$	88·08
$CaCO_3$	0·96
$CaCl_2$	0·45
$Ca(OH)_2$	6·74
H_2O not combined	3·77
	100·00

The small quantity of unchanged calcium hydroxide is proof for the opinion that this is merely lime mechanically protected against the action of chlorine by the bleaching compound $CaOCl_2$ previously formed.

The germicidal power of bleaching-powder solution is very great, and it has been used successfully for years as a disinfectant. One part of bleaching powder will, in 2–4 hours, destroy the following bacteria: coli, typhosus, and cholera in 2000 parts of ordinary sewage.

(*See* Schumacher, in Gesundheit-Ingenieur of Munich and Berlin, August 10, 19, 30, 1905; Sheridan Delépine, in Medical Chronicle, May, 1894; and G. C. Clayton, in J. Soc. Chem. Ind. 1896, 320.)

Calcium hypochlorite. The Chemische Fabrik Griesheim Elektron (D. R. P. 188524, 1906) describes the production of calcium hypochlorite as follows:—

Chlorine is introduced continuously with agitation into milk of lime until the latter is nearly saturated. The solution is then concentrated *in vacuô* until the calcium hydrochlorite crystallises out and can be dried *in vacuô*. The calcium hypochlorite obtained is said to be more stable than ordinary bleaching powder, gives a clear solution in water, and contains 80–90 p.c. available chlorine.

Liquid chloride of lime or Bleach liquor. Formerly many bleachers used to make their chloride of lime by passing chlorine gas into or over milk of lime. This is now done at such alkali works as are conveniently near bleach works, so that the cost of carriage of bleach liquor is not considerable.

On a laboratory scale the chlorine would be passed into the milk of lime. On the large scale this cannot be conveniently done, and is replaced by bringing the chlorine into contact with a

continually renewed surface of the absorbent. This might be done in towers on the principle of acid-condensers, but there are some drawbacks to this, and the general plan is to employ cast-iron vessels provided with mechanical agitators so constructed that the liquid is not merely circulating round and round, but that its surface is continually renewed. In most cases these are cylinders standing on their bases, with a vertical agitating shaft and horizontal arms; horizontal agitating gear is much more efficient, but is more troublesome, owing to the necessity of passing the axle through stuffing boxes in the sides of the vessel. Even with the ordinary upright cylinders, the absorption of chlorine is quite complete if three or more vessels are used in succession, so long as the agitator is at work, but the absorption ceases almost the moment the agitation ceases, from one cause or another.

In making bleach liquor, the agitators are charged with a milk containing about 1 to 1½ lbs. of slaked lime per gallon of water. The chlorine must not be evolved too fast, because this causes too great a rise of temperature. The rule is not to exceed 32°, or at most 37°; over this point the hypochlorite is very quickly changed into chlorate (cf. *Potassium chlorate*). It is very desirable that the absorbers should be surrounded by a cold-water jacket, to avoid that contingency. When the sp.gr. has risen to 1·040, the operation is stopped by turning the gas on to the next agitators; the first vessel, after the charge has been run off, and it has been refilled with fresh milk of lime, will now be the last of the series.

Well-finished bleach liquor contains a very small quantity of free lime, generally with a slight excess of $CaCl_2$ or of $Ca(ClO_3)_2$. The bulk of the chlorine is present as $Ca(OCl)_2+CaCl_2$.

The bleach liquor used, however, by bleachers is made, of course, in most cases by the solution of bleaching powder in water. This operation is quite simple, but to avoid at the same time a loss of available chlorine and a waste of time in settling out the excess free lime, $CaCO_3$ and insoluble matter, certain conditions have to be observed.

The conditions are that the temperature of solution should not be too low, and the agitation given too prolonged. A certain amount of agitation is necessary to avoid loss, but afterwards further agitation breaks up the aggregates of insoluble matter and delays the settling.

The following rules for making bleaching-powder solution have been found to work well in practice:—

1. The best practical temperature for the water is 21° to 26°.

2. The bleaching powder should be emptied into the agitating tank through a 1-inch mesh sieve, any lumps being knocked through with the flat of a spade.

3. The agitation should be performed so as to show a strong swirl on the surface, say, with a peripheral speed on the agitator of 500 feet per minute for tanks of 5 feet to 9 feet diameter, and the lower limbs of the agitator should be not more than 1 inch from the bottom of the tank.

After completing the volume of the bath, thorough agitation for 20 minutes is ample for all strengths of solution up to 16°Tw. Further time spent on agitation is wasted, and, by beating the bleaching powder, renders subsequent settling appreciably slower.

4. The run-off pipe should be at such a height as to allow 5 cubic feet of sludge per cwt. of bleaching powder used per batch, for all strengths of solution up to 16°Tw. Unless a sufficient space is allowed, enormous waste of time will arise in waiting for the last few inches to settle clear.

5. The sludge consists, not of bleaching powder, but of insoluble lime suspended in bleach solution. When the clear liquor has been run off, the agitating tank should be filled again with water, and the contents agitated for 5 minutes only prior to settling.

When the precautions given above are followed, the loss of bleaching powder in the washed sludge will not exceed 2 lbs. per cwt. of bleaching powder used, provided the last clear liquor is not more than 2°Tw.

Hypochlorite of potash (*Chloride of potash* or *Eau de Javel*). This liquor was first made in 1789 at the Javel Works near Paris, and was the first bleaching compound known. It was then made by passing chlorine into a solution of potashes (crude potassium carbonate) in eight parts of water. This liquor is rarely made at the present time, as it has been replaced by the cheaper soda compound, which has now mostly usurped its name.

Hypochlorite of soda (*Eau de Labarraque*, usually called *Eau de Javel*). This liquor can be made by passing chlorine into a solution of sodium carbonate in 10 parts of water till the liquid begins to effervesce and bleaches litmus. In that case it contains more or less free hypochlorous acid, according to the equations:

$$Na_2CO_3+2Cl+H_2O=NaCl+NaHCO_3+HOCl.$$
$$Na_2CO_3+4Cl+H_2O=2NaCl+CO_2+2HOCl.$$

The liquors containing free HOCl keep very badly, the HOCl partly volatilising and partly losing its oxygen.

Hypochlorite of soda solution is used to-day as a bleaching agent for the bleaching of special fabrics, in steam laundries to whiten clothes, and as a disinfectant.

For this purpose it is prepared either:

1. By the precipitation of a solution of bleaching powder by sulphate or carbonate of soda, when a solution is obtained containing about 5 p.c. of available chlorine, but no free HClO, and which will, therefore, keep unchanged for some time. This operation is usually conducted at the factory or the place where the solution is used.

2. By passing chlorine into a solution of caustic soda until nearly all the soda is chlorinated.

$$Cl_2+2NaOH=NaClO+NaCl+H_2O.$$

This solution is made commercially, and sold at a strength of 10–15 p.c. available chlorine.

It has been found necessary to leave a small amount of free soda, about ¼ p.c. Na_2O, in order to make the solution stable, and also to remove traces of iron which is converted into sodium ferrate, and aids the decomposition by carrying oxygen from the hypochlorite to the atmosphere. A very full statement on the manufacture and stability of sodium hypochlorite solution made in this way is contained in a paper by Muspratt and Smith (J. Soc. Chem. Ind. 1898, 1096).

3. By electrolysis of brine solution. Under chlorine we have discussed the electrolytic cells devised to liberate chlorine from common salt, and pointed out that the difficulties in designing an economic cell have been increased by the necessity for keeping separate the chlorine and soda produced. In this case no such necessity exists, and the chlorine is allowed to recombine at once with the soda produced, thus avoiding porous diaphragms and mercury cathodes, and decreasing the energy required by the energy of combination of chlorine and NaOH.

The following cells have been introduced (*see* papers by W. H. Walker in Electro-Chemical Industry, 1, 439):—

The Kellner cell consists of a stoneware vessel divided into a number of small compartments by glass plates fitting into small grooves in its sides. These glass plates are wound with platinum-iridium wire, and form bipolar electrodes. The electrolyte is circulated rapidly through the cell and through a cooling coil.

The Schuckert cell is a large stoneware trough, separated into 8–10 compartments. In these compartments are bipolar electrodes in the making of which platinum-iridium wire may or may not be used. Circulation is effected by means of the hydrogen evolved, and each cell has a cooling coil.

The Haas-Oettel cell consists of a rectangular box divided into small compartments by a series of vertical bipolar carbon electrodes set in grooves.

From the figures given by Walker, the k.w.h. per ton available chlorine produced in solution can be calculated, and are given in the following table for the Kellner and Schuckert cells. The Haas and Oettel figure is taken from a paper by Reuss before the Society of Dyers and Colorists, Feb. 1911:—

Name of cell	Details of a standard-sized cell		K.W.H. per ton available Chlorine
	Amps.	Volts	
Kellner . .	120	110	8800
Schuckert .	100	110	8500
Haas and Oettel	80	110	8400

These cells are adapted for the production of weak solutions only of hypochlorite of soda containing 1–2 p.c. available chlorine, as only a partial decomposition of the NaCl is possible without an enormous fall in efficiency. The cost of salt is, therefore, high, and actually about 7 tons of salt are required per ton of available chlorine produced.

Cells such as these are designed for the purpose of erection at the factory or works where the hypochlorite solution is used, usually with the object of displacing bleaching powder.

The figures given above for two items of cost alone (*i.e.* for power and salt) clearly indicate the reason why these ingenious pieces of apparatus have not attained a more extended use.

Hypochlorite of soda solution as a disinfectant. Hypochlorite of soda solution possesses strong germicidal powers, which Klein estimates for a solution containing 10 p.c. by weight of available chlorine at 21 times that of phenol. (*See* Klein, Comparative Bacteriological Report on Chloros, Public Health Engineer, June 9, 1906. Also for further data, *see* Schumacher, Gesundheit-Ingenieur of Berlin and Munich, Aug. 10, 19, 30, 1905; Clayton, J. Soc. Chem. Ind. 1896, 320.)

Solid sodium hypochlorite. Until recently sodium hypochlorite in the solid form was unknown. Muspratt and Smith, in 1898, however, by the systematic production of a more and more concentrated solution, produced crystals of the following composition (J. Soc. Chem. Ind. 1898, 1100):—

NaOCl	37·6 p.c.
$NaClO_3$	nil.
NaCl	3·7 „
Water (by diff.) . . .	58·7 „
	100·0

The crystals dissolve in their water of crystallisation at 18°–21°, and then rapidly decompose. By drying under vacuum part of the water of crystallisation is removed, and a more stable product obtained containing up to 60 p.c. of available chlorine with a melting-point of over 43° (*see* Muspratt, J. Soc. Chem. Ind. 1903, 592).

Bleach liquors containing magnesia, zinc, or *alumina,* all of them obtained by adding the sulphates of these bases to a solution of bleaching powder, are sometimes used for special purposes because they have a more rapid action than chloride of lime. Their properties have been fully investigated by Lunge and Landolt in the above-mentioned memoir. They are never manufactured for sale, but prepared by the users themselves.

Potassium chlorate. This salt is always manufactured by the process first indicated by Liebig; *i.e.* saturating milk of lime with chlorine under such conditions that calcium chlorate is formed, and afterwards decomposed by potassium chloride. For lime sometimes magnesia is substituted (*v. infra*). The reactions are:

(1) $6Ca(OH)_2+12Cl=5CaCl_2+Ca(ClO_3)_2+6H_2O.$

(2) $Ca(ClO_3)_2+2KCl=2KClO_3+CaCl_2.$

Hence only one-sixth part of the chlorine employed is, even by theory, converted into chlorate.

The first reaction is the formation of calcium hypochlorite and chloride, that is, ordinary bleach liquor; thus:

(3) $2Ca(OH)_2+4Cl=Ca(OCl)_2+CaCl_2+2H_2O.$

Under certain conditions the calcium hypochlorite is subsequently changed into a mixture of chlorate and chloride:

(4) $3Ca(OCl)_2=Ca(ClO_3)_2+2CaCl_2.$

There is, however, a concurrent change, which must be avoided, as it involves a great loss, namely, the splitting up of hypochlorites into chloride and oxygen:

(5) $Ca(OCl)_2=CaCl_2+2O.$

The conditions under which these changes occur, which were, of course, known in a general way before, have been exactly investigated by Lunge and Landolt (J. Soc. Chem. Ind. 1885, 722). They operated with a strong bleach liquor, composed according to the above equation (3). When gradually heated by itself up to 60° for 3 hours, this showed no perceptible change. Chlorate begins to be formed by

equation (4), when heated another hour to 70°, more so when heated another 2 hours to 90°; but even after 2 hours' full boiling (altogether 7 hours' heating), not much above ¼ of the available chlorine originally present has been employed for the production of chlorate, according to equation (4). Oxygen begins to be given off from the first, and in the end the reaction (5) prevails over (4). Hence the conversion of hypochlorite into chlorate by mere heating is a very unfavourable process.

A second way of converting hypochlorite into chlorate consists in saturating the solution with chlorine. This even at 15° causes 70 p.c. of the $Ca(OCl)_2$ to pass into chlorate. On gradually heating the solution, the reaction is quickened as soon as the temperature exceeds 40°, and it is complete at the boiling-point. Hence the presence of an excess of chlorine is a preventative against the reaction (5).

Most probably the excess of chlorine acts as follows:—

(6) $Ca(OCl)_2+4Cl+2H_2O=CaCl_2+4HOCl$.

(7) $2Ca(OCl)_2+4HOCl = CaCl_2+Ca(ClO_3)_2+4Cl+2H_2O$.

That is, the free chlorine acts only as a carrier of oxygen from two molecules of calcium hypochlorite upon a third; the first two are reduced to chloride, the third is oxidised to chlorate, and the free chlorine is fully regenerated in the end. The conclusions to be drawn for practice from Lunge and Landolt's experiments are as follows: The complete conversion of hypochlorite into chlorate is not effected either by mere heating or by a mere excess of chlorine, but both must act at the same time. A very large excess of chlorine is useless, perhaps even injurious. On the large scale the heat generated by the reaction suffices to complete the process.

Practically, chlorate of potash is manufactured in the following way.[1] Milk of lime is exposed to the action of chlorine in vessels provided with agitating gear, so that new surfaces are continually offered to the action of the gas, which in this case is quickly absorbed, and completely so if the gas partially taken up in the first vessels is ultimately brought into contact with fresh lime contained in the last vessel. Formerly the absorbing vessels were made of stone, in an octagonal shape, and hence were called 'octagons,' which name is sometimes even now used for the cylindrical cast-iron vessels which have universally displaced the real stone octagons. Such cylinders (shown in Fig. 28) are *e.g.* 10 feet wide and 5 feet 6 inches high, provided with a central vertical shaft *a* and agitating arms *b*, so contrived that they cause the liquid to well up and continually bring new portions of it to the surface. The shaft passes through an opening in the cover so constructed as to form a water-lute *c*, and a cup *d*, fastened on the shaft and dipping in the lute, prevents the escape of the gas round the shaft. Similar 6-inch lutes, *e*, *e*, serve for introducing and taking away the gas. There is also a manhole *f*, fitted with a cast-iron sleeve reaching 6 or 7 inches downwards, and forming a water-lute when the cylinder is filled. Apart from this the manhole is always open, so that observations can be made at any time, samples drawn, and hydrate of lime put in. Sometimes a water-jacket is applied outside. Three or (better) more cylinders form a set working together, so that the fresh

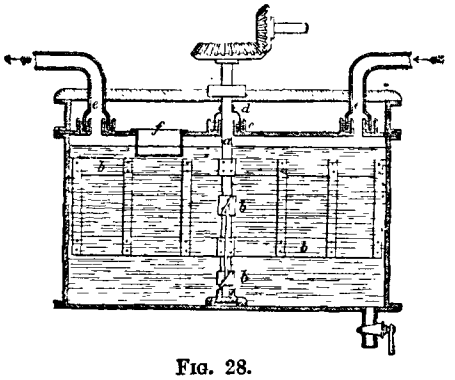


FIG. 28.

gas can be always turned upon that cylinder which is nearly finished, whilst the cylinder charged with fresh lime receives the last gas. From the last cylinder there should be pipes leading to a small box charged with hydrate of lime, in case of any accident happening to the agitating machinery, when the absorption of chlorine in the cylinders would very soon cease. In lieu of this, a column charged with milk of lime can serve as well.

The milk of lime must be prepared in such a way that the finished liquor becomes of a certain strength, which is, however, not the same at all works. The *sp.gr.* of the milk of lime itself should not exceed 16° or 17°Tw.; that of the finished liquor, 28° to 32°Tw. Some manufacturers go as far as 40°Tw.

The reaction causes an elevation of temperature, which up to a certain extent is useful; but it must not be allowed to get too high, because in this case oxygen is evolved, and there is a corresponding loss of chlorate. In no case can the theoretical proportion of 1 chlorate to 5 chloride be attained, as on the large scale, it appears impossible to entirely avoid some evolution of oxygen; but with good work the proportion can be kept at 1 : 5·3.

As the reaction proceeds, froth appears on the surface and the liquid becomes warm. In the first agitator the temperature should be from 65° to 70°; if it gets hotter, water-cooling is resorted to, or else the gas is cut off for a while. Afterwards the liquid turns pink, and the froth mostly vanishes again. The operation may be considered as finished when a sample taken out settles quickly and completely, leaving little sediment, smells of chlorine, and bleaches litmus paper. On adding hydrochloric acid *in the cold*, it should not give off chlorine (as hypochlorite would do). The pink colour is caused by calcium permanganate. The operation lasts from less than 24 hours to as long as 3 days, depending on the speed at which the chlorine is passed into the octagons.

The contents of each agitating vessel, as they are finished, are run into settlers provided with drop-siphons, and thence into special measuring tanks, from which the liquor is run into the concentrating vessels. In the measuring tank

[1] According to Dr. E. K. Muspratt (J. Soc. Chem. Ind. 1886, 408), this manufacture was commenced at St. Helens in 1847.

the volume and test are carefully noted to enable the quantity of potassium chloride (technically called muriate of potash) to be accurately calculated. The potassium chloride should be of the strongest kind (95 p.c.), and a small excess of it should be used. Some add it to the agitating vessels, under the (probably mistaken) idea that $KClO_3$ decomposes less easily than $Ca(ClO_3)_2$. Usually it is only added in the concentrating pans.

The mud left in the settlers is, of course, washed or filter pressed; the washings can be used for making fresh milk of lime.

The liquor as it runs away from the settlers still smells of chlorine. This is a nuisance, and it also acts upon the vessels, but the addition of a small quantity of a reducing agent like sodium thiosulphate, or even tank waste, entirely destroys the free chlorine.

The boiling-down pans are usually made of either wrought or cast iron, and are heated by direct fire. Since wrought-iron pans are not liable to crack, and are more easily repaired when partly worn out, they would seem preferable.

The boiling down is continued up to 70°Tw. (measured hot), in which case the mother liquors after crystallisation are not worth working up.

There is always a great deal of mud found in the pans, partly from incomplete settling, &c., partly formed by the action of the liquor on the metal. This mud must be removed by settling or by a filtering drum before running the liquor into the coolers.

The coolers for the first salts are generally made of iron, since in no case can a pure product be obtained at this stage. They are best made like those used for soda crystals, with a plughole for running off the mother liquor. They ought to be numerous enough to permit of the liquor remaining in them 9 or 10 days in winter and 14 days in summer. Here the crude chlorate of potash crystallises in long acicular crystals, totally unlike the thin plates in which the same salt crystallises when pure, but in reality possessing exactly the same faces, only developed in different fashion. They are easily distinguishable from the large transparent prisms of hydrated calcium chloride which appear if the concentration has been too great. They must be broken up after draining, and the adhering mother liquor washed off with a little water, and finally drained in a hydro extractor.

The mother liquor is a nearly saturated solution of $CaCl_2$, with a little KCl, and with about 30 grams of $KClO_3$ per litre. With bad work much more chlorate is left in the liquor. In the very best case 10–12 p.c. of all chlorate manufactured is lost through this cause, usually much more (25–30 p.c.). Usually it is not even attempted to recover the chlorine from these liquors by heating with hydrochloric acid—they are simply run to waste. But, with due care, the mother liquors can be quite well worked for chlorine by taking care to run the hydrochloric acid in *pari passu* with the liquor. Strictly speaking, it is not the chlorine of the chlorate which is recovered in this way, but chlorine produced by oxidation of the HCl added.

Wylde, Hammill, and Auer (Eng. Pat. 15097) describe a process for the recovery of about half the chlorate left in the mother liquor by refrigeration. The process is described in detail by Hammill (J. Soc. Chem. Ind. 1889, 168), who states that the crude crystals obtained by refrigeration have a finer grain than the ordinary crude crystals, but when thrown down from mother liquors of not over 72°Tw., are no more impure, and are as readily refined by one recrystallisation. Hammill says that on cooling to −12° only 13·5 grams $KClO_3$ per litre remain in the liquors. This process has now been worked successfully for many years.

The great loss of chlorate in the ordinary process has given rise to the process of Muspratt and Eschellmann, where magnesia is substituted for lime (Eng. Pat. 3960, 5183, and 5186 of 1883; and 1900 of 1885). A detailed description of this process has been given by Higgins (J. Soc. Chem. Ind. 1887, 248). The magnesia is obtained by burning Greek magnesite at not too high a temperature; when overburnt it is useless for the absorption of chlorine. The MgO is very finely ground, suspended in water, and exposed to the action of chlorine in the ordinary octagons. The reaction is not so violent as with lime. The temperature of a finished octagon is usually 43°, and it never exceeds 60°. In the finished liquor the proportion of chlorate to chloride is very near to the theoretical, viz. 1 : 5·1 or less; this constitutes an important advantage over the lime process, 7 p.c. less chloride being formed. No pink colour appears with very pure magnesia, but it does when it contains manganese. The strength of this liquor varies from 1·17 to 1·22.

The octagon liquor is now boiled down to 75°–80°Tw., when on cooling about 50 p.c. of the chloride will crystallise out as $MgCl_2,6H_2O$. The mother liquor contains I mol. chlorate to 2·8 chloride. Potassium chloride is now added to it in slight excess, and the potassium chlorate crystallised out. The mother liquors being much less in quantity than with lime, and $KClO_3$ being less soluble in $MgCl_2$ than in $CaCl_2$, the magnesia mother liquors contain much less chlorate than lime liquor (on an average 19 grams down to 10 grams per litre), and the yield of $KClO_3$ rises to 90 p.c. of the total.

The mother liquor is treated with HCl to destroy the chlorate, with due precautions against explosions. The still liquor is now neutralised with MgO; a solution of kieserite ($MgSO_4$) is then run in to decompose the calcium chloride present, and the gypsum, along with iron oxide, is settled out. The liquor is now concentrated in cast-iron pots (wrought iron is acted upon too much); the iron dissolving in the liquor is oxidised to the ferric state, and is precipitated by MgO; the settled liquor is run into barrels, where it sets to a hard mass containing 47 p.c. of $MgCl_2$. This magnesium chloride is sold to cotton sizers.

This process would, of course, only become general if the magnesium chloride obtained as a by-product could be profitably decomposed for chlorine, as it is not saleable by itself in very large quantities, and could not compete in price with the Stassfurt article.

Such utilisation for the manufacture of chlorine had been intended by Weldon, who first proposed magnesia for the above purpose, and it is again mentioned in a patent of J. Wilson

(5975 of 1884). Twynam (4397 of 1881) proposes dolomite, under the idea that double chloride of potassium and magnesium (carnallite) will crystallise out of the mother liquor after the chlorate. (This seems quite hopeless, since the principal question is not that of saving KCl, but $KClO_3$.)

Another process for greatly reducing the loss of chlorate in the mother liquors is that of Péchiney (*cf.* Weldon, J. Soc. Chem. Ind. 1882, 41). He concentrates ordinary chlorate liquor made from lime of a density of 25°Baumé, up to 48°B. (hot), and cools it down to at least 12°C., but not below 10°C. Of its 5·5 mols. of $CaCl_2$, 4·3 are thus caused to crystallise out as $CaCl_2,2H_2O$ (probably it should be $6H_2O$), but if the temperature were allowed to fall below 10°, calcium chlorate would crystallise as well. The crystals are separated by a hydro extractor, and the mother liquor is treated with the calculated quantity of KCl;[1] there being only 1·2 $CaCl_2$ present to 1 $KlCO_3$, the mother liquors cause a very much smaller loss than in the ordinary process. Péchiney's process is specially suited, and was originally invented, for the manufacture of sodium chlorate (*cf. infra*). It is evidently only possible to work it in the cold season.

The crude chlorate of potash is always purified by recrystallisation ('finished'). For this purpose it is redissolved in a mixture of water and of the mother liquor obtained in the finishing process, which is done in a lead-lined vessel, with the aid of steam, preferably indirect steam. The solution is made at a full boiling heat, sometimes with the addition of very small quantity of sodium carbonate and of sodium sulphide, in order to precipitate any iron and lead present; it is made up to 25°Tw., and, after good settling and straining through canvas, the liquor is run into the coolers. These are made of wood, or preferably iron lined with lead; they are either of a deep pattern, with wooden laths placed inside for the crystals to adhere to, or else they are made quite shallow, but covered over to prevent any too rapid cooling. The crystallisation lasts from 8 to 14 days, according to the season.

The crystals are drained, washed on the drainer, and then again drained in a hydro extractor. This is imperative, since it is required that chlorate of potash should show little or no trace of chlorides; 0·05 p.c. being a maximum sometimes stipulated. So long as there is $PbCl_2$ present, this cannot be very easily effected, but the lead can be removed in dissolving, as stated before. The mother liquors and washings are used over again till they become too impure, when they go back to the boiling-down pans. The crystals are dried on a hollow iron plate, covered with sheet lead, and heated by steam.

Chlorate of potash is either sold as 'crystals' or 'ground.' For the former purpose the crystals, as they come from the drying plates, are sifted through a sieve with eight holes to the linear inch, or less, as the case may be. The powder is best ground while still slightly warm. The mills may be of any description, horizontal, edge runners, rollers; but the chlorate during grinding ought not to come into contact with iron, nor with any organic substances (straw, wood chips, &c.), or dangerous explosions may occur. It must be sifted through a revolving sieve, made of miller's gauze, with mechanical brushes. The powder ought to be snow-white, and without any grittiness, like fine flour. The crystals ought to be in thin, brilliant transparent plates; excessive drying will make them opaque. Both are usually packed in 1-cwt. kegs, laid out with blue paper.

Formerly it was generally assumed that 1 part of chlorate of potash required 7 or 8 times as much chlorine as 1 part of bleaching powder, but with the new processes the yield is, of course, better than that. There is, however, even now a manufacturing loss of about 30 p.c. or at least 25 p.c. One ton of chlorate in the ordinary process requires, if the mother liquors are utilised for producing chlorine, about 30 tons of hydrochloric acid of 30°Tw., if the mother liquors are not so used, about 40 tons of acid will be used. This refers to Weldon chlorine; by combining the Deacon and Weldon process, and utilising the mother liquors as before, the consumption of acid ought not to exceed 22 tons. One ton of chlorate requires, moreover, 17–18 cwts. of 90 to 95 p.c. muriate of potash.

Chlorate of potash is principally employed for the manufacture of lucifer matches, for pyrotechnical purposes, for fuses, for some descriptions of gunpowder, and other cases where it is a constituent of explosive materials. It is also largely employed, on account of its oxidising properties, in dyeing and calico printing, in the manufacture of alizarin, &c.

Sodium chlorate. This compound, which formerly was only a chemical curiosity, has become of technical importance, since it was found that it is much more suitable for the preparation of aniline black than potassium chlorate, owing to its greater solubility.

At first when a demand for it sprang up, it was made from potassium chlorate by means of hydrofluosilicic acid (*cf.* Lunge's Alkali, 3, 320), and was sold at two or three times the price of the potassium salt. It was at that time thought that it could not be prepared from the calcium-chlorate liquor of the ordinary process, because $NaClO_3$ is very soluble, and cannot be separated from $CaCl_2$ by crystallisation. But this difficulty can be avoided, as we shall see.

The process of Bottomley and Molesworth (Pat. 3005 of 1881) consists in treating a hot saturated solution of potassium chlorate with one of bitartrate of soda, and separating the precipitated potassium bitartrate from the solution of sodium chlorate.

The real manufacture of chlorate of soda by a cheap process was first carried out by Péchiney, by means of his process of removing most of the calcium chloride from the crude liquor by crystallisation. The purified liquor thus accumulated during the colder part of the year is mixed with a solution of ordinary sodium sulphate, previously neutralised by lime. The operation is carried out in this way. An excess of solution of Na_2SO_4 is added to the chlorate liquor with continuous agitation; then more chlorate liquor is gradually run in, till the Na_2SO_4 has been completely converted into $CaSO_4$. The $CaSO_4$, which, under the

[1] The intermediate formation of a calcium oxychloride, described in Péchiney's patents and Weldon's paper, has since been given up.

proper conditions, is crystalline, is then separated from the liquor by filtration and washed in a hydro extractor. The solution of sodium chlorate is now concentrated by evaporation, during which most of the sodium chloride separates in the solid form and is fished out. The remaining solution on cooling yields crystals of sodium chlorate, which are purified by recrystallisation. After which the second crystals are washed. The mother liquor always goes back into the process. The purified salt contains no more than 0·16 p.c. NaCl. Nearly all the chlorate contained in the liquor is really obtained by this process, instead of the unavoidable loss occurring with chlorate of potash.

Chlorate of soda is also manufactured by the Muspratt Chlorate Process by means of their magnesium chlorate liquor, freed from nearly half the $MgCl_2$ by evaporation and crystallisation (*cf. supra*). To this liquor sodium carbonate is added, till all the magnesia is precipitated as a basic carbonate (magnesia alba), in order to be used over again in the process. The remaining solution of $NaClO_3$ and NaCl is concentrated by evaporation, with fishing out the NaCl, and after attaining 120°Tw., is allowed to cool down; the sodium chlorate crystallises out, and is purified in the usual manner.

Manufacture of alkaline chlorates by electrolysis. The passing of an electric current through a solution of NaCl or KCl liberates Na or K at the cathode, and Cl at the anode. The Na or K at once decomposes H_2O to form NaOH or KOH and hydrogen gas. If the electrolyte is heated from 45° to 100°, the Cl liberated is absorbed in the caustic alkali produced to form chlorate.

Theoretically, a current of 1 ampere will produce in 1 hour 0·7627 gram $KClO_3$, or 0·663 gram $NaClO_3$.

Gall and Montlaur, in their Eng. Pat. 4686 of 1887, describe the production of alkaline chlorates by the electrolysis of alkaline chlorides in a trough divided into two parts by a porous diaphragm.

The anodes are platinum-iridium sheets containing 10 p.c. of iridium; the cathodes are iron, though it is stated that nickel would be preferable.

The electrolyte consists of a 25-p.c. solution of KCl, kept at a temperature of about 80°. The liquor from the cathode compartment containing the alkaline hydrate there produced, is circulated through the anode compartment and combines with the chlorine liberated.

A current density of 50 amperes per square decimeter is used, and a pressure of 4·5 to 5·0 volts is required. In the case of potassium chlorate, the anode liquor is run into crystallising vessels, where the $KClO_3$ crystallises out, and the mother liquor, after resaturation with KCl, is passed back to the cathode compartment. In the case of sodium chlorate the anode liquor has first to be concentrated to crystallise out the NaCl before crystallising out the $NaClO_3$.

The crystals obtained require, of course, to be refined by recrystallisation, as in the case of those produced by chemical processes.

Hurter (Eng. Pat. 15396 of 1893) electrolyses KCl in a metal vessel which acts as cathode, and which has on its inner side a coating consisting of a mixture of Portland cement, salt and sand, which, after washing out the salt, yields a porous diaphragm. The anode is a sheet of platinum suspended in the centre of the vessel. Several vessels are superposed and worked in series, being kept apart by insulating rubber rings.

A solution of KCl containing a little caustic alkali is run into the top vessel, from which it overflows, through a glass or ebonite pipe, into the cell below. The hydrogen evolved escapes by pipes from the upper part of each compartment.

Blumenburg (Eng. Pat. 9129 of 1894) describes a cell with a porous diaphragm in which the anode compartment is closed and connected by a pipe with the bottom of the cathode compartment, so that the chlorine liberated at the anode passes into the liquor in the cathode compartment, and there combines with the caustic alkali produced, the temperature being maintained at a temperature of about 49°. In the Ger. Pat. 89035, and also in the U.S. Pat. 537179, Blumenburg passes the chlorine gases from the anode compartment into a gas holder, from which they pass to a separate combining vessel, where they are absorbed in the alkaline liquor from the cathode compartment. Chlorate is also formed as a by-product in the Griesheim cell described above, when using the oxide of iron anode.

In 1899 Imhoff made a great advance in the electrolytic production of chlorate by his discovery of the action of small quantities of chromate of potash or soda in the electrolyte (U.S. Pat. 627063 of 1899).

The action of the chromate is to prevent the reduction of hypochlorite and chlorate by the nascent hydrogen evolved at the cathode, and has resulted in a very marked and important improvement in the current efficiency.

The electrolytic manufacture of chlorates from chlorides was to commence with a simpler operation than the electrolytic production of caustic alkali and bleaching powder, owing to the fact that the products of the electrolysis do not require to be kept separate; and this fact, combined with the discovery of the use of alkaline chromates, caused the electrolytic chlorate industry to be successfully established some years before caustic soda and bleaching powder were economically manufactured electrically.

Hydrochloric Acid.

Commercial hydrochloric acid is a more or less pure solution of hydrogen chloride HCl in water.

Hydrogen chloride is a colourless gas, of sp.gr. 1·2596 (air=1), and molecular weight 36·457. By weight it consists of 2·74 parts of hydrogen and 97·26 parts of chlorine. It can be condensed into a liquid by cold and pressure; the tension of this liquid is 26·2 atmospheres at 0° and 40 atmospheres at 12·5°.

The heat of formation of a gram-molecule of HCl is 22001 cals.

Hydrogen chloride has a great affinity for water, and is greedily absorbed by it. The solution is the ordinary hydrochloric acid which, when somewhat concentrated, emits fumes of HCl on exposure to the air. The following table by H. Deicke shows the maximum solubility of HCl in water at varying temperatures. 1 c.c. dissolves at the temperature $t°$:—

	Vols. HCl at 0° and 760 mm. dissolved in 1 vol. H_2O	Specific gravity of the saturated solution	Percentage of HCl by weight in the solution
0°C.	525·2	1·2257	45·148
4	494·7	1·2265	44·361
8	480·3	1·2185	43·828
12	471·3	1·2148	43·277
14	462·4	1·2074	42·829
18	451·2	1·2064	42·344
23	435·0	1·2014	41·536

The behaviour of aqueous solutions of HCl under varying conditions of temperature and pressure has been principally studied by Roscoe and Dittmar (Chem. Soc. Trans. 12, 128). We shall mention here only the fact that concentrated hydrochloric acid on heating loses both gas and water, and gradually becomes weaker, until a sp.gr. of 1·101 and a percentage of 20·24 HCl is attained at a boiling temperature of 110°; the acid in this state distils without change, provided the atmospheric pressure is 760 mm. At a lower pressure the acid distilling unchanged is stronger, at a higher pressure it is weaker. A similar, but not identical limit is attained when strong acid is exposed to the air at ordinary temperatures.

The following table gives the percentages of HCl in aqueous hydrochloric acid at various specific gravities and at a temperature of 15°:—

Deg. Twaddell	Spec. gravity	Percentage of HCl	Grams HCl per litre	1 cubic foot weighs lbs.	1 cubic foot contains lbs. of HCl
1	1·005	1·12	11·32	62·66	0·70
2	1·010	2·12	21·45	62·97	1·34
3	1·015	3·12	31·67	63·29	1·97
4	1·020	4·11	41·99	63·60	2·61
5	1·025	5·11	52·41	63·91	3·26
6	1·030	6·11	62·93	64·22	3·92
7	1·035	7·10	73·55	64·53	4·58
8	1·040	8·10	84·27	64·84	5·25
9	1·045	9·10	95·09	65·16	5·93
10	1·050	10·09	106·01	65·47	6·61
11	1·055	11·09	117·02	65·48	7·31
12	1·060	12·09	128·14	66·09	8·00
13	1·065	13·08	139·36	66·40	8·69
14	1·070	14·08	150·68	66·71	9·40
15	1·075	15·08	162·10	67·03	10·11
16	1·080	16·07	173·62	67·34	10·83
17	1·085	17·07	185·24	67·65	11·55
18	1·090	18·07	196·96	67·96	12·28
19	1·095	19·07	208·78	68·27	13·02
20	1·100	20·06	220·70	68·59	13·76
21	1·105	21·06	232·68	68·90	14·51
22	1·110	22·06	244·80	69·21	15·27
23	1·115	23·05	257·02	69·52	16·04
24	1·120	24·05	269·34	69·83	16·79
25	1·125	25·05	281·76	70·14	17·57
26	1·130	26·04	294·28	70·46	18·35
27	1·135	27·04	306·90	70·77	19·14
28	1·140	28·04	319·62	71·08	19·93
29	1·145	29·03	332·44	71·39	20·73
30	1·150	30·03	345·36	71·70	20·54
31	1·555	31·03	358·34	72·02	22·35
32	1·160	32·02	371·44	72·33	23·16
33	1·165	33·02	384·64	72·64	23·99
34	1·170	34·02	397·94	72·95	24·82
35	1·175	35·01	411·34	73·26	25·65
36	1·180	36·01	424·84	73·57	26·49
37	1·185	37·01	438·44	73·89	27·34
38	1·190	38·01	452·14	74·20	28·20
39	1·195	39·00	466·00	74·51	29·06
40	1·200	40·00	479·84	74·82	30·00

The Manufacture of Hydrochloric Acid.

Practically all commercial hydrochloric acid is, and has been for a long period, produced by the decomposition of common salt in the manufacture of sodium sulphate or salt cake.

Owing to difficulties of transport in former days, small quantities of acid were produced locally by decomposing common salt with sulphuric acid in cast-iron cylinders.

In order to utilise the more expensive sulphuric acid, an excess of common salt was used. The solid product left in the cylinder consisted of sodium sulphate, mixed with 20–30 p.c. NaCl, and was commercially known as cylinder cake.

The production of hydrochloric acid from cylinders has, however, practically ceased, and the hydrochloric acid of commerce is distributed from centres where salt cake is manufactured, and is delivered to the customers in carboys or tank waggons.

Hydrochloric acid obtained in manufacturing sodium sulphate (salt cake). When salt was first decomposed in order to obtain sodium sulphate for the Leblanc process, the hydrochloric acid evolved during this process possessed no value, and was simply allowed to escape into the air. This continued to be the case even after that manufacture had attained a comparatively large extension, but the damage caused to the neighbourhood by the acid gases soon brought about the intervention of local authorities and courts of law, and manufacturers were compelled to seek means for condensing the acid. This was first successfully done by Gossage's coke towers in 1836, but in the great majority of works there was still a considerable loss of acid gases, as was proved by a Belgian Parliamentary Commission in 1856. But it is decidedly owing to Lord Derby's Alkali Act of 1863 (which has been followed by several other Acts) that British alkali makers were compelled, ultimately for their own good, to adopt thoroughly efficient means for condensing their hydrochloric acid, and this has benefited all other manufacturing countries as well.

In fact, the reports made by the inspectors under the Alkali Acts form an invaluable record of all the various steps taken for improving the condensation of hydrochloric acid, and these reports have helped to spread a better knowledge of that process and to cause manufacturers to improve it up to the highest standard of efficiency.

The Alkali Acts of 1863 made it incumbent upon those decomposing salt to allow no more

than 5 p.c. of the hydrochloric acid to escape into the atmosphere. An additional Act of 1874 prescribed that no more than 0·2 grain of HCl might be present in a cubic foot of the gas escaping from the factory into the air. This corresponds to 0·454 gram HCl per cubic metre, or about three ten-thousandths by volume. The latter clause applies to the chimney gases as well, and not merely to those escaping directly from the condensing apparatus. Although this requirement was at first declared by many to be impossible of fulfilment, the actual results proved at once that it was quite possible, and the escapes registered by the Alkali Inspectors have averaged far below the limits assigned by the Acts. Thus, in 1885, the average escape of HCl in chimney gases was 0·10 grain per cubic foot, or 2·39 p.c. Of the total amount produced in 1886, the figures were respectively 0·10 grain and 2·13 p.c. of the total hydrochloric acid.

Several further bills have become law since 1874, regulating the escape of other acid gases into the atmosphere, but no change has been made in the limit fixed in 1874 for escapes of HCl, viz. 0·2 grain HCl per cubic foot of chimney gas.

Although the various processes and apparatus used for the manufacture of sulphate of soda produce gases differing within wide limits in temperature and concentration of HCl, an efficient condensation, *i.e.* practically complete absorption of the HCl in water to form a liquid acid of 1·15–1·17 sp.gr. is usually obtained.

The efficiency of the condensation of gaseous HCl in water is dependent on three considerations:

1. Temperature.
2. Concentration of HCl in the gases to be scrubbed.
3. Time of contact.

On issuing from the sulphate of soda plant the acid gases require cooling. The apparatus used for this purpose depends on the temperature of the gases.

If the gases issue from the pot or pan of a handworked salt-cake furnace, the temperature is comparatively low. In this case the cooling is usually done in a row or rows of earthenware pipes. The pipes used are often unglazed, but are rendered impervious to moisture and gas by boiling in tar.

In some cases the earthenware pipes are substituted by glass pipes of 12 inches diameter, made slightly taper, as shown in Fig. 29. The glass pipes are, of course, more liable to breakages by accident, and also through the effect of violent changes of temperature than the earthenware pipes, but in sheltered positions they last well. For the hotter gases issuing from the furnace of an ordinary muffle hand sulphate of soda furnace, or from the cylinders of the Hargreaves process, cast-iron pipes are usually used to cool the gases down to a safe temperature before passing them as before into earthenware or glass pipes.

FIG. 29.

The action of the hydrochloric acid gases on cast iron, when at a temperature well above condensing-point of liquid acid, is very slight.

When open furnaces, whether 'hand' or

INFLUENCE OF TEMPERATURE ON THE SPECIFIC GRAVITY OF HYDROCHLORIC ACID.

0°	5°	10°	15°	20°	25°	30°	35°	40°	45°	50°	55°	60°	65°	70°	75°	80°	85°	90°	95°	100°
1·168	1·165	1·163	1·160	1·157	1·154	1·152	1·149	1·147	1·144	1·142	1·140	1·138	1·136	1·133	1·131	1·129	1·127	1·125	1·123	1·121
1·158	1·155	1·153	1·150	1·147	1·145	1·142	1·139	1·137	1·134	1·132	1·130	1·128	1·126	1·123	1·121	1·119	1·116	1·114	1·112	1·119
1·148	1·145	1·143	1·140	1·137	1·134	1·132	1·129	1·127	1·125	1·123	1·120	1·118	1·116	1·113	1·111	1·108	1·106	1·104	1·102	1·099
1·138	1·135	1·133	1·130	1·127	1·125	1·122	1·119	1·117	1·114	1·112	1·109	1·107	1·104	1·102	1·100	1·097	1·095	1·093	1·090	1·088
1·128	1·125	1·123	1·120	1·117	1·115	1·112	1·110	1·108	1·106	1·103	1·101	1·099	1·096	1·094	1·091	1·089	1·086	1·084	1·081	1·079
1·118	1·115	1·113	1·110	1·107	1·105	1·103	1·101	1·099	1·097	1·094	1·093	1·090	1·088	1·085	1·083	1·080	1·078	1·075	1·073	1·070
1·108	1·105	1·103	1·100	1·097	1·095	1·092	1·090	1·088	1·086	1·084	1·082	1·080	1·078	1·076	1·073	1·071	1·069	1·066	1·064	1·061
1·098	1·095	1·093	1·090	1·087	1·085	1·082	1·080	1·077	1·075	1·073	1·071	1·069	1·067	1·065	1·063	1·061	1·059	1·057	1·055	1·053
1·088	1·085	1·083	1·080	1·077	1·075	1·073	1·070	1·068	1·066	1·064	1·062	1·060	1·058	1·056	1·054	1·053	1·051	1·049	1·047	1·045
1·078	1·075	1·073	1·070	1·067	1·066	1·063	1·061	1·059	1·057	1·055	1·053	1·051	1·049	1·048	1·046	1·044	1·043	1·041	1·039	1·037
1·068	1·065	1·063	1·060	1·057	1·055	1·053	1·050	1·048	1·046	1·044	1·042	1·040	1·038	1·036	1·034	1·033	1·031	1·029	1·027	1·025
1·058	1·055	1·053	1·050	1·047	1·045	1·043	1·040	1·038	1·035	1·033	1·031	1·029	1·027	1·025	1·023	1·021	1·019	1·017	1·015	1·013
1·048	1·045	1·043	1·040	1·037	1·035	1·032	1·030	1·027	1·025	1·022	1·020	1·018	1·016	1·014	1·011	1·009	1·007	1·005	1·003	1·001
1·038	1·035	1·033	1·031	1·027	1·024	1·022	1·019	1·017	1·014	1·012	1·010	1·008	1·005	1·003	1·001	0·999	0·997	0·995	0·993	0·991
1·028	1·025	1·023	1·020	1·017	1·014	1·012	1·009	1·007	1·004	1·002	1·000	0·998	0·995	0·993	0·991	0·989	0·987	0·985	0·983	0·981
1·018	1·015	1·013	1·010	1·007	1·004	1·002	0·999	0·997	0·994	0·992	0·990	0·988	0·985	0·983	0·981	0·979	0·977	0·975	0·973	0·971

'mechanical' (such as the Mactear furnace), are used, the acid gases are mixed with the products of combustion, and are consequently both much hotter and more dilute.

Under these conditions extensive series of cast-iron pipes are used for the preliminary cooling before passing the gases into the earthenware pipes for final cooling.

The earthenware pipes used are usually 12-inch or 15-inch socket pipes, the joints being made with a cement of tar and China clay. The cast-iron pipes vary with the quantity of gas, and the arrangement of the cooling system of pipes from 12 inches to 20 inches; they are also usually socket pipes, the joints being made by ramming into the socket iron filings moistened with ammonium chloride solution.

The arrangement of the cooling pipes depends on the position of the different parts of the plant and the space available. When the salt-cake furnace is a long distance from the condensers, a single direct line of pipes may be not only the cheapest route, but a sufficient means of cooling.

Frequently where the distance is small the pipes are taken vertically up and down so as to obtain the necessary cooling surface. Usually the vertical columns of pipes start from and return to small stone cisterns.

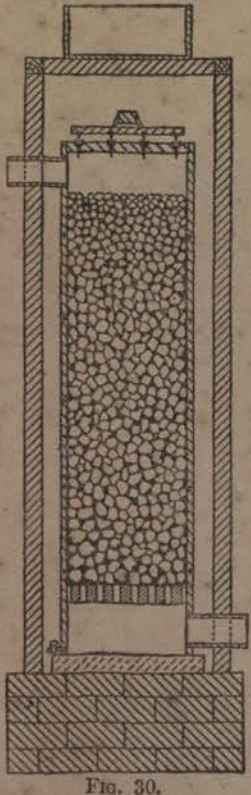


Fig. 30.

The cisterns are usually made in this country of silicious sandstone found in Yorkshire, and known as 'Yorkshire flag.'

The cisterns are composed of flags 4–6 inches thick, bound together by strong iron ties, and the joints made tight by thick indiarubber cord laid in a groove between the faces of the two stones, or by a mixture of tar and fire clay (*see* Figs. 31, 32, and 33).

After cooling the gases to a temperature varying in many cases from 25° to 45°, they are brought into contact with water, and scrubbed so as to completely absorb the HCl. The apparatus almost universally used are tall stone towers, packed with broken coke down which a stream of water is allowed to trickle, and up which the gases are caused to flow (Fig. 30).

These towers were invented and patented by Gossage, in 1836.

The coke tower has the merit of simplicity, and, when carefully packed, of efficiency.

The comparative efficiency of various modes of treating liquids with gases has been dealt with in a series of papers by Hurter, who also gives some interesting data on coke-packed towers (J. Soc. Chem. Ind. 1885, 639; 1887, 707; and 1893, 227 and 989).

Coke-towers are erections of stone, rarely of bricks or of acid-proof stoneware, in the shape of perpendicular shafts, mostly (except with pipes) of a square (for very wide towers of an octagonal) section, and of somewhat considerable height, varying from about 40 feet to 60 feet. The sectional area in the case of square stone or brick towers is rarely less than 5×5 feet, or more than 7×7 feet; but they have been made up to 14 feet diameter, of octagonal shape. They are provided with a grating a few feet over the bottom, on which rests the coke which forms the 'packing' of the tower. This coke, which must be of as hard a quality as possible (only the best oven-coke is applicable for this purpose), is disposed in such a way that the gas is as much as possible divided in a large number of channels (none of them being so wide that the bulk of the gas can pass up through it), and that the current of gas is constantly changed in direction. For this object long pieces of coke are laid parallel in a row; the next row is made to cross the lower one, and so forth. The size of the pieces is gradually diminished from bottom to top. In order to avoid an excessive quantity of the gas passing up the side of the condenser along the wall, it is usual to place a layer of finer coke round the condenser for a few inches from the wall. By this arrangement there is effected both a great division and constant mixture of the gases, and at the same time a suitable spreading of the feeding water over a very large surface. The water (or sometimes weak acid) is fed in at the top by some contrivance assuring a uniform distribution over the whole area of the tower; and in dropping down it keeps the irregular surfaces of the coke moist all over, thus presenting a very large area of contact between the gases and the liquid. In consequence of the large area of the tower, and the number of changes of direction the gases have to make while passing through it, they are ultimately deprived of all their soluble parts, consisting principally of hydrochloric acid, and leave the tower in a state fit to be discharged into the atmosphere without any damage to the neighbourhood.

It is, however, necessary that a condenser should fulfil certain conditions, if it is to do its work properly. In the first instance, its size must be proportionate to the work done; if the gases pass too rapidly through it, there will not be time enough to effect a complete washing out of the acids. Everything depends upon the way in which the condenser is packed, on the regularity of work in this pan and furnaces, on the proper regulation of the feed, on the draught, even upon the outward atmospheric conditions, and it is unnecessary to say that nothing like the same amount of condensing space in the shape of coke towers is required if the main work of condensation has been previously done by cooling pipes, cooling towers, and Woulfe's bottles.

Of recent years there has been a growing tendency in England to do away with all cooling

pipes, cisterns, wash towers, &c., and to adopt the system of very large stone towers to do the whole work of condensation for two or even more pots and furnaces.

The condensers are practically always worked two in series, the weak acid from the second condenser or final scrubber being run down the first or strong condenser. In this way complete absorption of the acid is assured, with production of a strong liquid acid, *i.e.* one of over 1·15 sp.gr. A common practice is to work two condensers in series of about 5×5×50 feet high to condense the acid from two-hand salt-cake furnaces.

No difficulty is now experienced in pumping the weak acid made in the second condenser on to the top of the first condenser, and the following apparatus is used for the purpose:—

Stoneware ram pumps, ebonite ram pumps, stoneware acid eggs, and occasionally even yet the Hazlehurst membrane pump, patented in 1876.

The ascension pipe is usually of stoneware or ebonite, occasionally of lead.

Brick towers are not to be recommended, as it is practically impossible to keep the numerous joints tight against acid oozing out. Columns

Fig. 31.

of stoneware pipes cannot be made of a large area, and, therefore, are not very well adapted to large works, at least if intended for coke towers; but they do very good service at smaller works, or as supplementary to a large condensing plant of stoneware receivers. The material mostly employed for coke towers is acid proof sandstone or, in France, volvic lava, just as for acid tanks. The system of joining the flags together is the same as shown in Figs. 31 and 32 or Fig. 33; but there is also another system shown in Fig. 34, in which the flags are kept

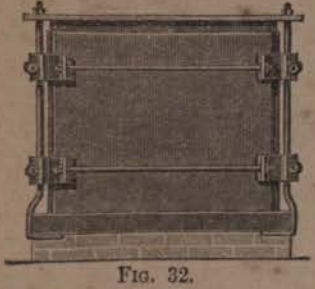


Fig. 32.

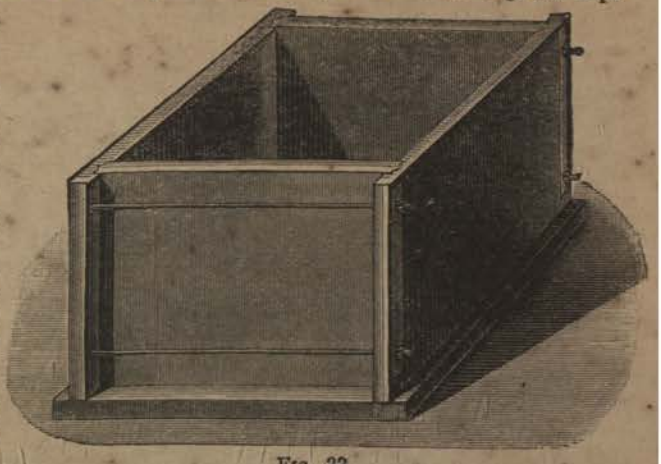


Fig. 33.

together by means of *grooves worked in* the stone, and without the aid of any ironwork, which is always a source of anxiety in acid condensers.

The coke towers are generally placed at a

Fig. 34.

high level, and are, if necessary, put upon pillars, for the purpose of running the acid from them by gravitation either into chlorine stills, or into store cisterns for sale. They must, of course, have a very secure foundation, in the construction of which not merely the great weight of the tower must be considered, but also the probability that there will be now and then leakages of acid which may soften the ground and make the

foundation unsafe. This can be avoided by asphalting the ground in such a way that any acid running down cannot penetrate into the soil, and is conveyed to a safe distance. Any damage done to the foundation, even if it amounts to much less than would cause the erection to break down altogether, is extremely injurious, because it will almost unavoidably lead to the tower getting out of level, in which case the gases will always tend to rise on the higher side, and the water will principally descend on the lower side; thus the necessary contact is not attained, and the action of the condenser is most injuriously affected.

It has been already stated that the feeding of the condenser with water must take place in such manner as to supply the whole area of it with moisture. This can be done in various ways. The plan formerly considered as most efficient is that of a distributing wheel (shown in Figs. 35 and 36) worked by the pressure of the feed water

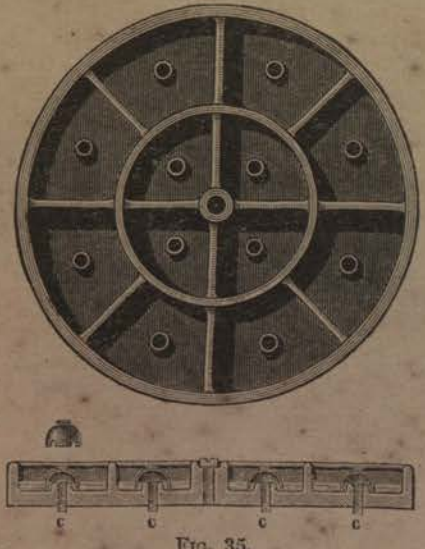


FIG. 35.

itself. This causes the stream of water to reach successively every one of the holes on the top of the condenser, and thus secures a uniform action without depending upon the top of the tower being at a mathematical level. Recently most manufacturers have done away with these acid wheels, and have introduced troughs provided with a number of overflows all at the same level, feeding the same number of 'lutes,' C, C. This arrangement is indicated on Fig. 30, p. 39.

Since 1836 a number of suggestions have been made of apparatus to replace partially or altogether the Gossage coke tower.

These suggestions have, in most cases, been confined to different arrangements of packing the tower so as to expose a larger surface of water to the gas than is exposed by the broken coke. Of these we may mention the Lunge Rohrman plate tower (Figs. 37, 38, and 39).

The Lunge Rohrmann plate tower consists of a tower packed with a series of perforated plates E, E, the perforations being made to alternate in successive plates, so that each hole corresponds to a solid place in the plates just above and below.

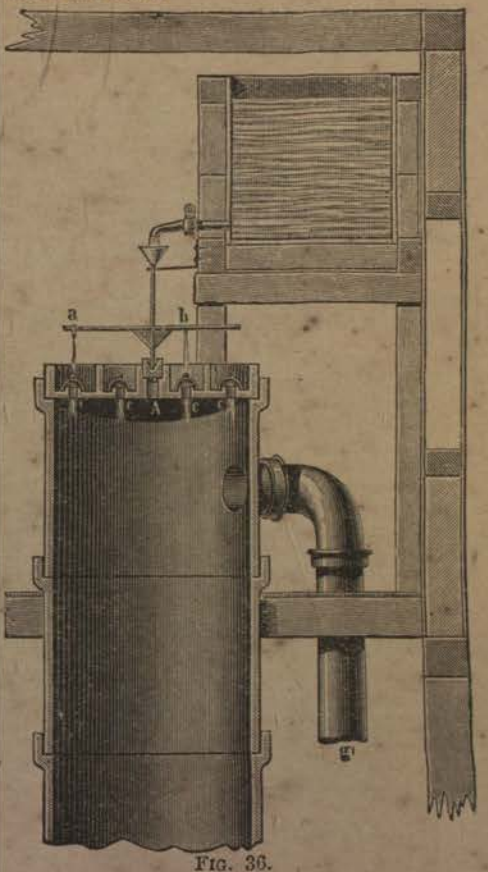


FIG. 36.

Figs. 38 and 39 show one of the plates in

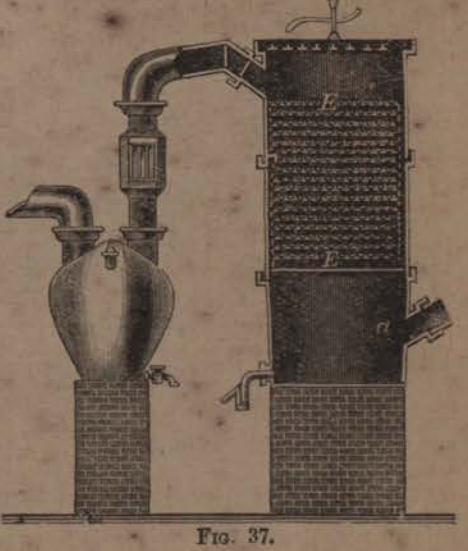


FIG. 37.

detail. As is to be expected, the evidence for and against the improved packings for the condensing towers is very conflicting, and as the cost of them is naturally higher, the coke-packed tower has fully maintained its position.

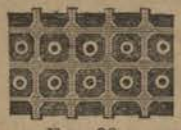


FIG. 38.

FIG. 39.

One great advantage the coke-packed tower has is that, owing to the porous nature of the coke, it always retains a large store of water and liquid acid, usually several hours' supply, which tends to keep the condenser steady under a fluctuating flow of HCl, and to tide over difficulties occasioned by a stoppage or breakdown of the water supply.

In France and Germany a somewhat different system of cooling and condensation is in general use.

The earthenware and glass pipes mentioned above as being used almost exclusively in this country for the final cooling of the gases are, at any rate, partially substituted by a series of earthenware Woulffe's bottles, known technically as bombonnes or touries (*see* Fig. 40). A long row or sometimes two parallel rows are arranged so that the acid gases pass onward from the furnace through the pipes *b*, *b*, and the liquid acid

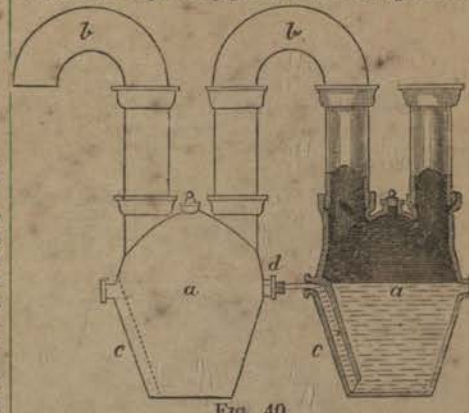


FIG. 40.

flows in the opposite direction, entering each receiver through the pipe *c* and overflowing at *d* into the next jar. In passing through the bombonnes, the weak acid absorbs a large proportion of the HCl passing over it, and, in spite of the relatively high temperature in the leading bombonne, eventually gives a liquid acid of 1·15–1·18 sp.gr. The size of the bombonnes varies from about 50 to 100 gallons, rarely more and rarely less, and the number employed in a set varies from 40 to 100. The jars should be of the best stoneware, which is able to stand somewhat violent changes of temperature. After leaving the bombonnes, the acid gases are finally scrubbed with water in a coke-packed tower or condenser, similar in design but usually

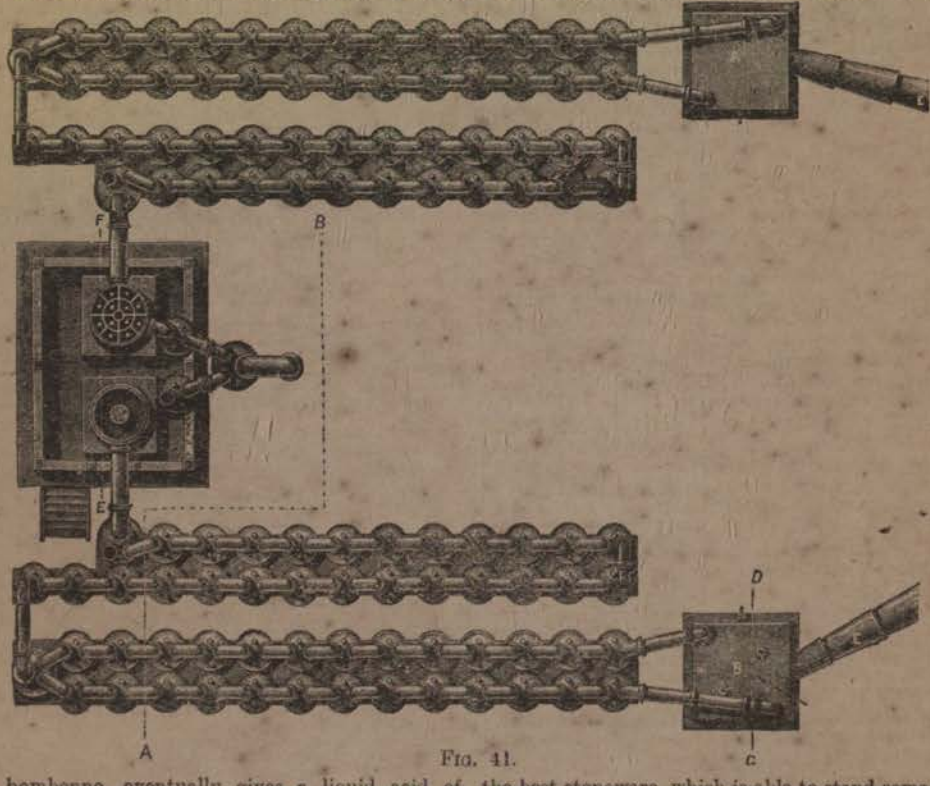


FIG. 41.

much smaller than those used in this country. The weak liquid acid produced in this tower supplies the stream of weak acid required by the bombonnes.

Fig. 41 shows a whole set of receivers as arranged for the gases from a salt-cake pot and furnace with a small coke tower to give the final scrubbing.

In the condensation of hydrochloric acid gas in water with the apparatus at present used and described above, there is little reason for difficulty in avoiding losses of HCl through incomplete absorption. The difficulty more commonly experienced is to combine the complete absorption enforced by law with a high-strength liquid acid.

The working of the condensing plant. Success depends first on sufficient time of contact for the gases to reach a state of equilibrium with the issuing liquid acid under their actual condition of temperature and gaseous concentration; and secondly, on having the gases sufficiently cooled before coming in contact with the liquid acid to keep down the temperature inside the condenser. The actual temperature admissible depends on the gaseous concentration of the HCl entering the condensing apparatus, but, as mentioned previously, frequently varies between 25° and 45°.

The impurities found in commercial hydrochloric acid are, chiefly, sulphuric acid, ferric chloride, arsenic, and either free chlorine or sulphurous acid. The acid condensed from the pan or pot gas is always much purer than that from the roaster gas. The quantity of *sulphuric acid* in the gases from the salt-cake furnace sometimes amounts to 2 p.c. and upwards; it is very troublesome in the Weldon, and fatal in the Deacon, chlorine process, and in some other applications of hydrochloric acid. The sulphuric acid in the salt-cake furnace gases can be removed to a large extent by a small condenser or dry scrubber before condensation.

A large number of suggestions have been made for the purification of the salt-cake furnace gases, so as to render them suitable for the Deacon process, but the only one of these processes to achieve practical success is the Hasenclever process (Eng. Pat. 3393 of 1883). (*See* Deacon Chlorine Process.)

Arsenic gets into the hydrochloric acid through the sulphuric acid employed in its manufacture; the arsenic is thereby converted into $AsCl_3$, and passes as such into the condensing apparatus. Many plans have been proposed for its removal—most frequently a treatment with sulphuretted hydrogen or with sulphides. Bettendorf (Dingl. poly. J. 194, 253) precipitates the arsenic from concentrated hydrochloric acid by stannous chloride, distilling it afterwards. Duflos dilutes the acid to sp.gr. 1·13, and digests it with strips of sheet copper at 30°C. for 24 hours, and repeats this treatment with freshly scoured copper. This removes all the arsenic and the free chlorine, and reduces the ferric chloride to ferrous chloride, which remains behind on distillation. Beckurts (Fischer's Jahresb. 1884, 348) distils hydrochloric acid with ferrous chloride and removes the first 30 p.c. containing all the arsenic.

Even *selenium* is sometimes found in such quantities in hydrochloric acid as to be troublesome in its application (Davis, J. Soc. Chem. Ind. 1883, 157).

Hydrochloric Acid from other Sources than the Leblanc Process.

Attempts have been made to produce hydrochloric acid from many sources, notably from the residual liquors of the ammonia-soda process.

A number of suggestions have been made for the direct production of HCl: 1st, from $CaCl_2$; 2nd, from $MgCl_2$; 3rd, from NH_4Cl.

In this connection compare the references given for the production of chlorine from these bodies earlier in the article.

As far as is known, none of the processes is used.

Hydrochloric acid from the ammonium chloride of the ammonia-soda process (*cf.* this for many details). Mond (1883) heats the ammonium chloride with so much sulphuric acid that the acid sulphate is formed and all HCl is expelled. The acid sulphate is converted by means of ammoniacal vapours into the neutral salt of commerce. O. N. Witt (1886) expels the HCl from NH_4Cl by means of syrupy phosphoric acid, which forms ammonium phosphate. On heating this at a higher temperature, the ammonia is driven out as well, and the phosphoric acid is regenerated. Jurisch (Dingl. poly. J. 267, 431) has shown that this process is not practicable, because there is no material known which resists the fusing phosphoric acid, and only 63 to 86 p.c. of the NH_3 is recovered.

Mond passes the vapour of ammonium chloride over nickel oxide, heated to at least 350°, which absorbs the HCl and allows the NH_3 to pass on. After a certain time the process is changed by raising the temperature to 500° or 600° and decomposing the nickel chloride by steam, when HCl is driven off and NiO regenerated. (Several patents taken out in 1886.)

The *conveyance* of hydrochloric acid mostly takes place in glass carboys with basket or wire hampers, sometimes in earthenware carboys of the same size (about 10 or 12 gallons). At a large French works, some years ago, tank waggons were used, carrying iron cylinders lined with ebonite.

Tank waggons for hydrochloric acid, have of late years, come into general use, especially on the Continent.

The tank waggons usually consist of a waggon platform, carrying a number of stoneware jars of about 1 ton capacity each jar. Fig. 42 shows

Fig. 42.

such a waggon carrying 12 jars of 1 ton each, or 12 tons of acid altogether. Specially prepared wooden tanks are also used occasionally.

The *applications* of hydrochloric acid are very numerous, but most of it serves for producing chlorine. The acid is also used for

preparing the chlorides of various metals; for extracting the phosphates from bones, &c.; for purifying bone-char (it must be quite free from sulphuric acid for this purpose); in dyeing and tissue printing; for preparing carbonic acid; for neutralising the alkaline 'melts' in the manufacture of alizarin, resorcin, &c.; in manufacturing many other coal-tar colours; and for innumerable other purposes. A. C.

CHLOROBENZENE *v.* PHENYL.

***p*-CHLOROBENZENE DIAZOCYANIDES** *v.* DIAZO- COMPOUNDS.

CHLOROFORM, *Trichloromethane* $CHCl_3$.

Chloroform was discovered by Liebig in 1831 (Pogg. Ann. 23, 442), and independently, about the same time, by Soubeiran (Ann. Chim. Phys. [2] 48, 131). Besides its well-known use as an anæsthetic, for which purpose it was introduced by Simpson in 1848 (Edin. Monthly J. Med. Sc. 8, 415), it is largely employed as a solvent in chemical manufactures and as a valuable antiseptic.

Formation.—1. By the action of alkalis on chloral: $CCl_3{\cdot}CHO+NaHO=CHCl_3+HCOONa$ (Liebig, Pogg. Ann. 23, 442; Annalen, 1, 199; 162, 161).—2. By acting on alcohol with bleaching powder. The bleaching powder probably, in the first instance, converts the alcohol into aldehyde, then into chloral, liberating calcium hydroxide, which latter, reacting on the chloral, converts it into chloroform and calcium formate:

(*a*) $CH_3{\cdot}CH_2{\cdot}OH+CaOCl_2=CH_3{\cdot}CHO+H_2O+CaCl_2$.
(*b*) $2CH_3{\cdot}CHO+3CaOCl_2=2CCl_3{\cdot}CHO+3Ca(OH)_2$.
(*c*) $2CCl_3{\cdot}CHO+Ca(OH)_2=2CHCl_3+(HCOO)_2Ca$.

(Liebig; Soubeiran, Ann. Chim. Phys. [2] 48, 131; Soubeiran and Mialhé, Annalen, 71, 225.) A very similar reaction takes place when a mixture of alcohol and an alkaline chloride is submitted to electrolysis, whereby chloroform is also produced (Patent, J. Soc. Chem. Ind. 1885, 243). Methyl cannot be substituted for ethyl alcohol in these processes, for it yields no chloroform when treated with bleaching powder (Belohoubek, Annalen, 165, 349).—3. Chloroform is produced by the action of chlorine or bleaching powder on acetone or acetic acid (Liebig) or acetophenone (Orndorff and Jessel, Amer. Chem. J. 10, 363). With acetone the reaction is

$$2CO(CH_3)_2+6CaOCl_2=2CHCl_3+2Ca(OH)_2+3CaCl_2+(CH_3COO)_2Ca$$

(O. and J.).—4. By heating trichloroacetic acid with water, alkalis, or ammonia

$$CCl_3{\cdot}COOH+H_2O=CHCl_3+CO_2+H_2O$$

(Dumas, Ann. Chim. Phys. [2] 56, 115; Annalen, 32, 101; Beckurts and Otto, Ber. 14, 589).—5. Chloroform is also produced by acting upon turpentine and the terpenes with bleaching powder (Chautard, J. 1851, 501).—6. By the action of nascent hydrogen on carbon tetrachloride (Geuther, Annalen, 107, 212).—7. Together with methylene chloride by treatment of methyl chloride with chlorine in sunlight (Regnault, Annalen, 33, 328).—8. From iodoform by the action of phosphorus pentachloride (Gautier, Bull. Soc. chim. [2] 13, 127).

Manufacture.—Chloroform is chiefly prepared by distilling a mixture of bleaching powder, water, and alcohol, with or without the addition of slaked lime. The diluted alcohol is warmed in a still to which a condenser is attached, and then the bleaching powder and lime are added, and the temperature raised till chloroform begins to come over, after which the heat evolved by the reaction itself suffices to complete the distillation. Sometimes an evolution of oxygen has been noticed during the progress of the reaction. This arises from decomposition of part of the bleaching powder by heat (Bechamp, Ann. Chim. Phys. [5] 22, 347). Operators differ as to the best proportions of alcohol and bleaching powder to be employed (*cf.* Kessler, J. Pharm. Chim. [3] 13, 162; Simmerling, Arch. Pharm. [2] 53, 23; Belohoubek, *l.c.*; Brit. Pharm. 1885, 108). For small quantities, the directions of the above Pharmacopœia may be followed. The apparatus used for manufacturing on a larger scale usually consists of a generator with an attached condenser and receiver, a washing apparatus and tanks, all made of iron, and a copper still for the final rectification (*cf.* Chem. Zeit. 10, 338). The generator is cylindrical, 1·4 m. high, and 2 m. in diameter, and is constructed of boiler plate 13–14 mm. in thickness. It is fitted with an agitator, a manhole through which the charge is introduced, a tube 75 cm. in diameter connecting with the condenser, and two other tubes, the one for the introduction of water and the other for steam. A tube, closed at the lower end, passes through the plate and filled with oil holds a thermometer. There is also arranged, outside the generator, a leaden tube connected with the water supply, by which a small current of water can be spread over the generator, when, as sometimes occurs, the temperature of the reaction rises too high. The tube leading to the condenser should be short, and should have as great a dip as possible. Between the condenser and the receiver is inserted a piece of glass tubing, by means of which the evolution of chloroform may be observed. The receiver is a cylindrical tank made of boiler-plate about 15 mm. in thickness and is about 75 cm. high and 40 cm. in diameter. The washing apparatus consists of a narrow high cylinder with a rounded bottom in which is fitted an agitator in the shape of a ship's screw. This, when working, keeps up a movement of the liquid from below upwards. Taps are placed in the sides to draw off the alcoholic washings. The final rectification is conducted in a copper still, the arm of which, leading to the condenser, is made as short as possible.

Three parts of 85 p.c. alcohol diluted with 60 parts of water are added to the generator, and then, while the agitator is in motion, 12 parts of bleaching powder, which should contain not less than 35 p.c. of available chlorine. Steam is applied till a temperature of 40° is obtained, when it is shut off. The temperature still rising, the agitator is stopped when about 45° are indicated, after which the heat of the reaction causes a further increase in temperature which generally does not exceed 60°. If it should rise higher than 60°, the cooling apparatus must be made use of. The beginning of the reaction is marked by a fine rain of chloroform, alcohol and water being driven rapidly through the condenser tube, and the air contained in the apparatus being energetically expelled. The chloroform soon follows, the agitator being set in motion to assist towards the close of the distillation. When the product, on being examined,

ceases to separate in layers, when, in fact, it consists of a solution of chloroform in alcohol, it should be collected separately. This is continued until, on the addition of water to the distillate, no further separation of chloroform takes place. After the chloroform has all come over, a quantity of weak spirit is recovered. The crude chloroform is then thoroughly washed in the washing apparatus, and finally rectified from the copper still. The washings, together with the various spirituous distillates, are utilised in subsequent operations (*cf.* Chem. Zeit. 10, 338).

In England, chloroform is prepared not only from 'rectified spirit,' but also from the duty-free 'methylated spirit,' a mixture of rectified spirit with 5 or 10 p.c. of wood naphtha. The latter product can be sold at a much lower price than the former. It has been doubted whether it is applicable to purposes of inhalation, but the weight of evidence is in favour of the view that 'methylated' chloroform when properly purified may be employed as an anæsthetic with precisely the same degree of safety as chloroform prepared from rectified spirit. Indeed, it seems impossible, either chemically or physiologically, to distinguish the one from the other.

Other reactions employed for the manufacture of chloroform are: the action of bleaching powder on acetone, of which method particulars are given with drawings of apparatus by Sadtler (Pharm. J. [3] 20, 84); the electrolysis of solutions of chlorides of the metals of the alkalis or alkaline earths in alcohol or acetone, the whole being kept heated during the operation (Patents, J. Soc. Chem. Ind. 1885, 243; 1896, 959; 1901, 148; 1904, 536); the destructive distillation of acetates, and subsequent treatment of the distillate with hypochlorite (Patent, J. Soc. Chem. Ind. 1885, 611); and from carbon disulphide by the formation and subsequent reduction of carbon tetrachloride (J. Soc. Chem. Ind. 1896, 555, 612; 1904, 383).

The chloroform prepared by any of the above-mentioned processes is not of so high a degree of purity as that produced by the action of alkalis on previously purified chloral, and requires purification before it is adapted for purposes of inhalation. The first step is usually to wash it with water, which removes traces of ethyl alcohol. Then it is left for a short time in contact with sulphuric acid (Gregory, Proc. Roy. Soc. Edin. 1850, 391), which must be free from nitrous compounds (*cf.* Christison, Pharm. J. 10, 253; Redwood, Year Book of Pharmacy, 1870, 119). This acid has no action on chloroform itself unless the operation be unduly prolonged, but it chars most of the impurities which are commonly present. In the next place, the product is allowed to stand in contact with recently ignited sodium carbonate (*cf.* Thorpe, Chem. Soc. Trans. 37, 196), or with oxide of manganese, or it is washed with lime water and afterwards dried over calcium chloride. In any case, it is finally distilled at a temperature not above 64° (*cf.* Werner, Arch. Pharm. [3] 12, 450; Thorpe, *l.c.*; Remys, Arch. Pharm. [3] 5, 31; Michaelis and Mayer, Dingl. poly. J. 261, 496).

Other methods of purification are by freezing (Eng. Pat. 15514, J. Soc. Chem. Ind. 1892, 59), on cooling to −80°, foreign bodies crystallising above this temperature can be removed, the temperature is then reduced to −82°, when pure chloroform crystallises and may be separated; and by means of the compounds formed by chloroform with salicylide or *o*-homosalicylide (Anschutz, Annalen, 273, 94). These, on gentle heating, give off pure chloroform.

Chloroform is liable to decomposition in presence of air and sunlight. Among the products formed are hydrochloric acid and chlorine (Marson, Pharm. J. 8, 69; Abraham, *ibid.* 10, 24), and sometimes carbonyl chloride (Regnauld, J. Pharm. Chim. [5] 5, 504). Such decomposed chloroform may be purified by washing with sodium thiosulphate and subsequent distillation (Shuttleworth, Pharm. J. [3] 3, 1016; *cf.* Remys, Arch. Pharm. [3] 5, 31). The addition of 1 p.c. of ethyl alcohol is largely practised to prevent the decomposition of chloroform. This somewhat retards the formation of carbonyl chloride and hydrochloric acid, but does not altogether prevent it. Carefully purified sulphur effectually prevents decomposition. No impurities could be detected in a sample treated in this way after four months' exposure to sunlight (Allain, Chem. Zeit. 19, 310). Breteau (Fr. Pat. 353858, 1905; Breteau and Woog, Compt. rend. 143, 1193) gives a list of substances which also prevent the decomposition of chloroform by air and light.

Properties.—Chloroform is a liquid having a sweet taste and an agreeable ethereal odour. When inhaled it produces anæsthesia. As an antiseptic it prevents the growth of micro-organisms, but does not affect the action of soluble ferments (*cf.* Patent, J. Soc. Chem. Ind. 1886, 331). (For antiseptic applications, *v.* Robin (Compt. rend. 30, 52), Augendre (*ibid.* 31, 679), Barnes (Pharm. J. [3] 5, 441), Salkowski (Chem. Rep. 1888, 166); also Pharm. J. [3] 18, 315, 356 and 855.) Chloroform is very sparingly soluble in water; 1 vol. dissolves in 200 (*cf.* Chancel and Parmentier, Compt. rend. 100, 773). It mixes in all proportions with alcohol or ether. It may be made into an emulsion with water by means of saponin (Patent, J. Soc. Chem. Ind. 1887, 382). Sulphuric acid does not dissolve it. Chloroform is an important solvent; dissolving fats, resins, indiarubber, sulphur, phosphorus, iodine, alkaloids, many alkaloidal salts, as well as numerous other organic compounds (*cf.* Pettenkofer, J. 1858, 363; Schlimpert, *ibid.* 1859, 405; Nowak, Arch. Pharm. [3] 3, 281; Hesse, Pharm. J. [3] 4, 649).

M.p. −70° (Berthelot, Bull. Soc. chim. [2] 29, 3), −60·2° (Haase, Ber. 26, 1053). B.p. 61·2° (corr.) Thorpe (Chem. Soc. Trans. 37, 196; *cf.* Regnault, J. 1863, 70); Pierre (Ann. Chim. Phys. [3] 33, 199); Schiff (Annalen 220, 95). Sp.gr. 1·52637 at 0/4 (Thorpe, *cf.* Pierre; Schiff). V.D. 4·199 (Dumas), 4·230 (Regnault). Coefficient of expansion, 0·0012302 (Thorpe).

Chloroform is not inflammable even with a wick at ordinary temperatures. It may, however, be made to burn, with a green smoky flame when boiling, or by means of a wick when diluted with alcohol. Heated to redness, its vapour is decomposed, yielding chlorine and various chlorides Ragsky, J. pr. Chem. 1849, 46, 170; Ramsay and Young, J. Soc. Chem. Ind. 1886, 232). By treatment with zinc and sulphuric acid, methylene chloride CH_2Cl_2 is formed; with alcohol or

ammonia and zinc-dust, methane (*cf.* Perkin, Chem. News, 18, 106); with alcoholic potash, formate and chloride (Regnault), together with carbonic oxide (Geuther, Annalen, 123, 121), or in closed tubes, ethylene (Berthelot, Ann. Chim. Phys. [3] 54, 87); with alcoholic potash in presence of monamines, *iso*nitriles (Hofmann, Ber. 3, 769); with sodium ethoxide, methenyltriethylic ether $CH(OEt)_3$ (Kay, Chem. Soc. Trans. 1855, 7, 224); with concentrated hydriodic acid when heated, methylene iodide CH_2I_2 (Lieben, Zeitsch. Chem. [2] 4, 713); with red-hot copper (Berthelot, Compt. rend. 1, 805) or potassium amalgam (Kletzinsky, Zeitsch. Chem. [2] 2, 127), acetylene C_2H_2.

Chromic acid converts chloroform into phosgene $COCl_2$. Repeatedly distilled in a current of chlorine, hydrochloric acid and carbon tetrachloride are formed (Regnault). Ordinary nitric acid has little or no action (Soubeiran), but fuming acid in closed tubes at 100° slowly converts it into chloropicrin $C(NO_2)Cl_3$ (*cf.* Mills, Chem. Soc. Trans. 24, 641). Bromine and iodine derivatives, *v.* Paternò (Gazz. chim. ital. 1, 593), Friedel and Silva (Bull. Soc. Chim. [2] 17, 537), Bolas and Groves (Chem. Soc. Trans. 9, 779). Sodium reacts on chloroform in contact with atmospheric air, forming formate and chloride together with free carbon and other products (Kern, Chem. News, 31, 121). Potassium decomposes chloroform vapour with liberation of carbon and formation of chloride (Liebig; *cf.* Heintz, Pogg. Ann. 98, 263). Potassium hydroxide solution has no action on chloroform even when boiled with it; but heated in closed tubes, formate and chloride are formed (Dumas). Similar products, together with carbonic oxide, are obtained by treatment of chloroform in closed tubes at 180° with ammonia and water (André, Compt. rend. 102, 553). At a red heat ammonia reacts on chloroform, forming hydrocyanic and hydrochloric acids (*cf.* Heintz). Chloroform combines with sulphuretted hydrogen and with water at 0°, forming the crystalline compounds $CHCl_3(H_2S)_2(H_2O)_{.3}$ (Loir, J. 1852, 560; Forcrand, Ann. chim. Phys. [5] 28, 12); and $CHCl_3(H_2O)_{18}$ (Chancel and Parmentier, Compt. rend. 100, 27).

The following reactions have been made use of in the detection or estimation of chloroform: —1. The reaction between chloroform and monamines in presence of alcoholic potash. A small portion of the liquid to be tested is added to a mixture of a monamine—aniline, for instance—together with some alcoholic potash, and heat applied, when, if traces even of chloroform are present, the characteristic disagreeable odour of an *iso*nitrile is distinctly perceived:

$$CHCl_3+NH_2Ph+3KHO=Ph(NC)+3KCl+3H_2O.$$

This test, which serves to distinguish one part of chloroform in 5000–6000 of alcohol, further distinguishes between chloroform and its allied derivatives such as ethylidene chloride $CH_3{\cdot}CHCl_2$ (Hofmann, Ber. 3, 769).—2. A delicate colour reaction takes place between potassium phenate and chloroform. An alcoholic solution of phenol is mixed with potassium hydroxide and evaporated to dryness. If chloroform be now added, a splendid red-purple colour is developed (Guareschi, Gazz. chim. ital. 1873, 401; Raupenstrauch, Pharm. J. [3] 19, 668).—3. If chloroform be added to a solution of caustic soda with an excess of resorcinol, and heat be applied to boiling, a yellow-red colour is developed which, when largely diluted, shows a yellowish-green fluorescence (Schwarz, Zeitsch. anal. Chem. 27, 668; Raupenstrauch).—4. α- or β- naphthol, dissolved in concentrated potassium hydroxide solution, and warmed with a little chloroform, gives a rich blue liquid which changes in the air to green and brown (Lustgarten, Monatsh. 3, 715).—5. Fehling's solution is reduced by chloroform, thus:

$$CHCl_3+2CuO+5KHO=Cu_2O+3KCl+K_2CO_3+3H_2O.$$

This reaction furnishes a means of indirectly estimating chloroform (Baudrimont, J. Pharm. Chim. [4] 9, 410).—6. (For the estimation of chloroform in alcoholic solution, *v.* Thresh (Pharm. J. [3] 11, 319).)—7. Chloroform is detected in blood by distillation from a water-bath, and its decomposition into chlorine and other products when the gases evolved are led through a tube heated to redness. The liberation of chlorine is observed by its action on starch and iodide of potassium paper (Ragsky, *l.c.*; Duroy, J. Pharm. Chim. [3] 20, 401; Ludeking, Chem. News, 55, 149).—8. To detect it in cases of fatal poisoning, Vitali distils the intestines and passes hydrogen through the distillate. The hydrogen, carrying with it portions of any chloroform which may be present, is burned at a jet and in the flame is fixed a copper wire. Very minute quantities of chloroform generate hydrochloric acid in the flame sufficient to act on the copper and impart a bright-green colour (Gazz. chim. ital. 1881, 489).—9. (For applications of the naphthol colour test to forensic analysis, *v.* Lustgarten (*l.c.*).)

Detection of Impurities.—Chloroform for inhalation should leave no residue or unpleasant odour on evaporation, should be neutral to test-paper, and give no indication of hydrochloric acid when tested with silver nitrate. A much more delicate method of detecting free acid is to add to 5 cc. of chloroform 1 drop of a solution of phenolphthaleïn and 1 drop of a centi-normal solution of potassium hydroxide with 1 c.c. of water. The mixture is shaken and set aside. If free from acid, the red colour should not disappear in 24 hours (Vulpius, Arch. Pharm. [3] 25, 998). The presence of alcohol in chloroform may be detected by the darkening in colour of sulphuric acid shaken with it (Gregory, Proc. Roy. Soc. Edin. 1850, 391); by the formation of iodoform (Hager, Pharm. J. [3] 1, 683); by the tint of the solution which it gives with iodine (Siebold, *ibid.* [3] 10, 213); by the addition of Hofmann's violet, which is quite insoluble in pure chloroform (Regnauld, J. Pharm. Chim. [4] 29, 402); by its reducing action on an alkaline solution of potassium permanganate (Yvon, J. Pharm. Chim. [5] 5, 225) or manganate (Jolles, Chem Zeit. 11, 786 and 1394), or on chromic acid (Cottell, J. Pharm. Chim. [3] 13, 359). The fact that chloroform for inhalation purposes usually contains alcohol, purposely added to increase its stability, materially lessens the value of these tests in practice (*cf.* Dott, Pharm. J. [3] 12, 769). Aldehyde may be detected by many of the tests for ethyl alcohol, and also by warming with potassium hydroxide, when its presence is indicated by a darkening in colour (*cf.* Regnauld, *l.c.*; Scholvien, Pharm. Zeit. 32, 686).

A. S.

CHLOROPHENINE ORANGE *v.* AZO-COLOURING MATTERS.

CHLOROPHENINE YELLOW *v.* PRIMULINE AND ITS DERIVATIVES.

CHLORORUBINE *v.* MADDER.

CHOCOLATE is a mixture of cacao paste with sugar and flavouring matter. The paste is prepared from fermented cacao beans (the unfermented kinds being unsuitable for chocolate making) in the manner described under COCOA. The sugar, which constitutes 50 p.c. or more of the mixture, consists usually of white crystals (although the lower-grade coloured sugars may be used for the cheaper chocolates), ground to the finest powder and completely dried before admixture with the cacao paste. The most common flavouring substance is vanilla, but other spices, as cardamoms, cinnamon, cloves, mace, and nutmeg, or the essential oils extracted from them, also artificial flavourings such as vanillin, are frequently employed. Peru balsam and gum benzoin are sometimes used for a similar purpose. The flavourings are introduced either in alcoholic solution or incorporated with sugar moistened with a little oil.

It is essential that during admixture the paste should be kept in a liquid condition, and to this end the mixing machines are heated to a temperature slightly above the melting-point of cacao butter, say from 35° to 40°, and the added sugar may be previously warmed with advantage to obviate a fall in temperature of the liquid cacao paste.

The various characters of French, Spanish, Swiss, and other chocolates depend upon the nature and proportions of the different ingredients used. A number of recipes for the preparation of some of the principal types of chocolate are given in Zipperer, 156.

In addition to sugar, various farinaceous substances are frequently employed in the cheaper forms of chocolate, as wheat and potato flour, rice, arrowroot and dextrin, and occasionally barley, oats, rye, and chestnut flour. In special cases where sugar is inadmissible, as in chocolate intended for use by diabetic subjects, the sugar is replaced by saccharin (*q.v.*). It is then usual, in order to give the necessary 'body' to the chocolate, to add some form of meal or flour (preferably leguminous); and pea, bean, or linseed meal are preferred for this purpose. *Nut chocolate* is made by adding nuts, either ground or whole, to the chocolate paste; and *milk chocolate* by incorporating with it 'milk powder,' *i.e.* milk deprived of its moisture and fat. The usual composition of milk chocolate, by the best makers, is approximately 10 p.c. cacao, 25 p.c. cacao butter, 40 p.c. sugar, and 25 p.c. dried milk. The above-mentioned forms of chocolate, after being ground into a more or less homogeneous mass, are placed in moulds to form bars, blocks, cakes, and numerous fancy shapes.

An immense variety of fancy preparations of chocolate consist, however, merely of a chocolate envelope containing other substances, as biscuits, creams, dried fruits, nuts, fruit jelly, liqueurs, &c., and in some cases, medicinal preparations, as chocolate-coated pills. The most important of these fancy preparations are the chocolate creams.

The so-called 'cream' is made either from powdered loaf sugar heated until it melts, or a mixture of this with glucose, with or without various colouring and flavouring materials. While in a liquid state, it is poured into moulds of the desired shape, made in starch flour on a table, which can be kept cool and which can be agitated by mechanical means. On cooling, the creams set into a stiff granular mass, when they are either dipped into a liquid chocolate paste, or the latter is poured over them by hand and spread uniformly by means of the rocking table. The process of covering, as well as most of the other processes in the manufacture of chocolate, are now generally effected by means of ingenious and complicated machinery.

An extra amount (about 15 p.c.) of cacao butter (or substitute) is added to the chocolate intended for covering purposes, to keep the latter in a sufficiently plastic condition during the process of cooling and to give smoothness to the finished article. The latter, whether in the form of plain chocolate or chocolate confections, should be quickly cooled, and attention to temperature is important throughout all the various operations.

The adulterants commonly used in chocolate are similar to those mentioned under COCOA, the most important being the replacement of the cacao butter by other fats and oils (as coco-nut fat, illipé butter, &c.), the addition of various farinaceous substances, including dextrin, and the admixture of finely ground cocoa shells. (Zipperer, Die Shokoladen Fabrikationen; Villiers et Collin, Traité des Substances Alimentaires.)

J. C.

CHOCOLATE FATS. Under this name, the writer comprises those vegetable fats which are used in the manufacture of chocolate as cacao butter substitutes. The natural chocolate fat is cacao butter, and best chocolates contain cacao butter only. 'Cheap' chocolates are made, to a larger or smaller extent, if not entirely, with substitutes. At first, animal fats were used, but as they impart an unpleasant flavour ('animal flavour') to the chocolate, at present fats of vegetable origin only are employed, such as coco-nut stearine and palm-nut stearine. During recent years, attempts have been made to produce chocolate fats from Borneo tallow, dika fat, and similar vegetable fats.

J. L.

CHOLESTEROL. Discovered by Conradi, in 1775, in gall-stones. Found in human bile, in blood, and in the brain; in epidermis and in hair; also present in various morbid products of the animal body, *e.g.* cerebral concretions, scirrhous matter of the mesocolon, hydropic liquid of the stomach, testicles, &c. Also found in horn and hoofs; in whalebone, tortoiseshell, feathers and bristles, &c. Its most abundant source is, however, the fat of greasy wool (wool grease), in which it was first detected by Hartmann and Schulze.

It is separated from the fatty acids in wool grease by distillation with superheated steam or by direct heating. Distillation is continued until the yellow granular distillate, consisting chiefly of fatty acids, begins to go brown. The residue is a black-brownish product and is mainly cholesterol (Mayer, Eng. Pat. 20639; J. Soc. Chem. Ind. 1894, 162). It is also prepared from animal and vegetable substances

rich in lecithin (Fischer, Eng. Pat. 11597; Fr. Pat. 390683; J. Soc. Chem. Ind. 1908, 176). Lifschütz has obtained it in small quantities by oxidising oleic acid with potassium permanganate (Chem. Soc. Abstr. 1908, i. 263).

Cholesterol crystallises in thin white nacreous monoclinic laminæ, m.p. 145° and of sp.gr. 1·067. Has a neutral reaction, and is without taste or smell; insoluble in water; sparingly soluble in cold but readily dissolved by boiling alcohol. Also soluble in ether, chloroform, acetone, wood spirit, benzene, oil of turpentine, and in the neutral fats and fatty acids. Sublimes unchanged at 200°, but is decomposed at a higher temperature. Cholesterol appears to be an alcohol containing two double linkages, and combines with the fatty acids, forming esters or compound ethers similar to the glycerides, but whether it should be represented by the formula $C_{26}H_{44}O$ or $C_{27}H_{46}O$ is still under discussion (Windaus, Arch. Pharm. 1908, 117; Mauthner and Suida, Monatsh. 15, 362; Diels, Ber. 1908, 544, 2596; Molinari and Fenaroli, Ber. 1908, 2785).

Detection.—By evaporating a weak ethereal solution of the substance, adding 3 drops of an alcoholic solution of benzaldehyde and 1 drop of conc. sulphuric acid, and gently warming, a reddish-violet colour is soon produced, changing after a short time to a deep violet, if cholesterol is present (Chem. Zeit. 1899, [3] 21). Another method is to dissolve the substance in anhydrous acetic acid, add excess of acetyl chloride and a few lumps of zinc chloride. In the presence of cholesterol, the solution assumes a reddish colour, and has a greenish-yellow fluorescence, the colour being deepest after five minutes' boiling. This reaction will detect 1 part of cholesterol in 80,000 (Tshugaieff, J. Soc. Chem. Ind. 1900, 933). Lifschütz (Ber. 1908, 252) dissolves a few milligrams of the substance in glacial acetic acid, adds a few particles of benzoyl peroxide and 4 drops of conc. sulphuric acid. If cholesterol is present, a blue-green or violet colour is produced, changing on standing through green to violet.

Estimation.—Lewkowitsch (J. Soc. Chem. Ind. 1897, 134) estimates cholesterol by obtaining its saponification value and its iodine absorption value in the usual way. Ritter (Chem. Zeit. 1901, 872) heats 50 grams of the fat on the water-bath with 100 c.c. alcohol, and when boiling, adds a hot solution of 8 grams of sodium in 160 c.c. of 99 p.c. alcohol. The alcohol is evaporated off and 75 grams of salt added and sufficient water to dissolve the contents of the basin. Evaporate to dryness and complete in an oven at 80°. The mass is pulverised and extracted in a Soxhlet apparatus with ether, the ether extract bring transferred to an Erlenmeyer flask. The extraction flask is washed out with ether, the combined extract and washings being evaporated to dryness and the residue dissolved in as little alcohol as possible. The flask is gradually filled with water, the precipitate being filtered off and dried at 60°. When dry, it is extracted with ether, transferred to a weighed flask, the ether evaporated off, the residue dried at 100°–120°, and weighed (*v.* also Oils and Fats).

Cholesterol is found in commerce under the name of lanolin, and is used mainly for medicinal purposes, and, owing to the ease with which it is absorbed by the skin, as a substitute for vaseline, or lard, in the composition of plasters, ointments, and salves. It has also been employed in the manufacture of cosmetics and pomades, and for softening leather. Lanolin is obtained from wool oil, which contains about 70 p.c. of cholesterol and 30 p.c. fatty acids, by saponification by means of caustic soda, whereby an emulsion is obtained which on dilution with water gives so-called 'wool milk.' On treatment in a centrifugal machine, impure lanolin separates out as a cream, and may be precipitated by lime. The purified product is afterwards kneaded with about 30 p.c. of water, in which state it is found in commerce.

Anhydrous lanolin absorbs about 100 p.c. of water, does not become rancid, and is antiseptic.

CHOLESTROPHAN *v.* Parabanic acid.

CHOLINE $C_5H_{15}NO_2$, *Hydroxyethyl-trimethyl-ammonium hydroxide* $CH_2(OH)\cdot CH_2\cdot N(CH_3)_3OH$, occurs in many animal and vegetable tissues. It has been found in the brain, in egg-yolk, in putrefying horse-flesh, in the seeds of the vetch (*Vicia sativa*), fenugreek (*Trigonella fœnum græcum*), the pea (*Pisum sativum*), and hemp (*Cannabis sativa*); in seedlings of wheat, barley, the pea-nut, lupines, soy-beans, and cucumber; and in the cakes left in the extraction of cocoa-nut oil, palm oil, sesamé oil and cotton-seed oil.

In addition to its occurrence as the free base in the products mentioned, it is present in many animal and vegetable substances in the form of lecithin (*g.v.*). Choline may be obtained from aqueous extracts of plant or animal tissues by adding lead acetate, filtering, removing the excess of lead by sulphuretted hydrogen, evaporating the filtrate to dryness, extracting with alcohol, and precipitating with alcoholic mercuric chloride solution. The mercuric double chloride is recrystallised, dissolved in warm water, and the mercury removed by sulphuretted hydrogen, the filtrate is then evaporated and the hydrochlorides left are treated with cold alcohol in which the choline salt dissolves, leaving the betaine hydrochloride (often present with the choline) undissolved (Schulze, Zeitsch. physiol. Chem. 1909, 60, 155).

Choline can be synthesised by the action of trimethylamine on a strong solution of ethylene oxide (Wurtz, Annalen, Suppl. 6, 201):

$$C_2H_4O+H_2O+N(CH_3)_3 = CH_2(OH)\cdot CH_2\cdot N(CH_3)_3OH$$

Choline is a syrupy liquid with a strongly alkaline reaction. It forms a crystalline chloride which is readily soluble in alcohol and gives crystalline compounds with platinum tetrachloride or gold trichloride. It forms a precipitate with potassium triiodide in alkaline solution.

Choline acts as a poison, and to its presence in cotton-seed cake the injurious effects which this food has upon young animals and especially upon pigs, are probably due. The typical effect of choline upon the animal body is a lowering of the arterial blood pressure (Mott and Halliburton, Proc. Physiol. Soc. 1899, 9; also Abderhalden and Müller, Med. Klinik. 1910, No 22; and Mendel and Underhill, Zentr. Physiol. 1910. 24, 251) H. I.

CHONDRIN. A substance allied to and much resembling gelatin. Obtained by boiling

cartilage with water. When dried it is a hard, horny substance which softens to a jelly in cold water, and is entirely dissolved by boiling water. It is precipitated from its aqueous solution by nearly all acids, in excess of certain of which it redissolves; and by alum, lead acetate, copper and iron suphates, and mercuric and mercurous nitrates. These reactions are said to distinguish it from gelatin.

By Morochowitz, chondrin is regarded as a mixture of gelatin, mucin, and salts (*v.* GLUE).

CHROMATOMETERS *v.* COLORIMETERS.

CHROMAZONE BLUE, -RED *v.* AZO- COLOURING MATTERS.

CHROME-BLACKS, -DEEP BLACK, -BROWNS, -FAST BLACK, -FAST CYANINE, -FAST YELLOWS, -YELLOW, -ORANGE, -PATENT GREEN *v.* AZO- COLOURING MATTERS.

CHROME VIOLET. Syn. *Mauveine, Perkin's violet* (*v.* AZINES AND COLOURING MATTERS). The term is also applied to the sodium or ammonium salt of aurintricarboxylic acid (*v.* AURIN, and TRIPHENYLMETHANE COLOURING MATTERS).

CHROMITE or Chrome-iron-ore. A member of the spinel group of minerals, consisting essentially of ferrous oxide and chromic oxide $FeO{\cdot}Cr_2O_3$, or $FeCr_2O_4$, analogous to the aluminates. The ferrous oxide is, however, often partly replaced by magnesia, and the chromic oxide by alumina, so that there is a passage to chrome-spinel or picotite; on the other hand, with a replacement of chromic oxide by ferric oxide, there may be a transition to magnetite (Fe_3O_4 or $FeFe_2O_4$). All these minerals are cubic in crystallisation and belong to the same isomorphous group—the spinel group. The actual amount of chromic oxide varies considerably, as shown by the following analyses; the ordinary ore, as mined, contains on an average 45 p.c. Cr_2O_3:—

	Cr_2O_3	Al_2O_3	Fe_2O_3	FeO	MgO
I.	67·9	—	—	32·1	—
II.	44·15	22·41	5·78	11·76	15·67
III.	59·20	7·15	n.d.	25·02	4·42
IV.	41·23	24·58	2·28	16·99	14·77
V.	56·54	12·13	—	18·01	14·08

I. Calculated for $FeCr_2O_4$.
II. Franklin, Macon co., North Carolina.
III. Price's Creek, Yancey co., North Carolina (J. H. Pratt, Amer. J. Sci., 1899, vii. 281). Also SiO_2 2·80, MnO 0·69.
IV. Tampadel, Lower Silesia (H. Traube, Zeits. Deutsch. Geol. Ges. 1894, xlvi. 50).
V. Dun Mountain, New Zealand.
(For analyses of chromite isolated from meteorites, *see* W. Tassin, Proc. U.S. Nat. Museum, 1908, xxxiv. 685.)

In general appearance, chrome-iron-ore is very like magnetite, but it is readily distinguished from this by the dark-brown colour of its streak or powder, and by the fact that it is only slightly, if at all, magnetic. Sp.gr. about 4·5. Crystals are of rare occurrence, the mineral being usually found as grains disseminated in basic rocks of igneous origin, especially those rich in olivine (viz. the peridotites). Sometimes these grains are segregated into nodular masses of considerable size and with a granular to compact texture. Rocks of this kind, when subjected to weathering processes, become hydrated and altered into serpentine, and for this reason most of the workable deposits of chrome-iron-ore are in serpentine-rocks. With the denudation and breaking down of these rocks, the heavy grains of the chemically resisting chromite collect in the beds of streams and rivers; and some of the deposits worked in the Ural Mountains are of this nature.

Chromite is the only commercial source of chromium and its compounds. It is used for the preparation of the oxides and chromates employed as pigments, and in dyeing, calico-printing and tanning; in the manufacture of chrome-steel, and for chrome-bricks and furnace linings. It is mined in European and Asiatic Turkey, Greece, the Ural Mountains, New Caledonia, India, Rhodesia, and Quebec; and formerly, to a considerable extent, at Bare Hills, near Baltimore in Maryland, and in Lancaster co. in Pennsylvania. Quarries were, at one time, worked on Unst, one of the Shetland Isles. The world's output amounts to about 80,000 tons per annum. L. J. S.

CHROMIUM. (Fr. *Chrome*; Ger. *Chrom.*) Symbol Cr. At. wt. 52·0. Chromium occurs principally as chrome-iron-ore, or *chromite* (*q.v.*). As sesquioxide Cr_2O_3, it is found in small quantities in *chrome ochre*, generally mixed with clay and associated with chromite, in France and Siberia. As lead chromate it occurs in *crocoisite* and *malanchroite* $PbCrO_4$, and as a basic lead chromate in the rare mineral *phœnicite* $3PbO{\cdot}2CrO_3$. It is usually present in the form of *chromite* in meteorites, but rarely to the extent of more than 1 p.c. The greenish colour of the emerald, verd-antique marble, serpentine, sapphire, and many other minerals, is due to the presence of chromium sesquioxide.

Preparation.—Metallic chromium may be prepared by several methods. Deville produced it in combination with a small quantity of carbon, in ingots weighing as much as 100 grams, by the ignition of a mixture of chromium sesquioxide and sugar in a lime crucible, at the highest temperature of a blast furnace.

Wöhler (Annalen, 111, 230) prepared chromium by fusing a mixture of the violet chromium sesquichloride with twice its weight of zinc under a layer of equal parts of potassium and sodium chlorides. The mixture of zinc and chromium so produced was treated with dilute nitric acid to remove the zinc, and the chromium remained as a light-greenish powder consisting of minute octahedra belonging to the quadratic system (Bolley), of sp.gr. 6·81 according to Wöhler, 7·3 according to Bunsen.

Chromium may be prepared by the electrolysis of its salts, but the purity and condition of the deposit vary greatly with current strength and solution concentration. A bright deposit, capable of receiving a polish, can be obtained by the use of a hot 25 p.c. acid solution of chromic chloride, with a current density of about 40–50 amperes per square foot. As in the case of nickel, the deposits have a strong tendency to peel (Cowper Coles, Chem. News, 81, 16).

It is most easily obtained in small quantities by heating equivalent parts of chromic oxide (or mixture of the oxide and anhydride) with aluminium powder. When started, the heat of the reaction causes it to continue and a fused mass of chromium of a high degree of purity is obtained (Goldschmidt, Annalen, 301, 19).

In large quantities it is best prepared by heating the oxide with carbon in the electric furnace. The crude metal thus obtained always contains *carbides*, of which two definite compounds appear to exist: Cr_3C_2 and Cr_4C. It may be refined by further heating in the electric furnace on a bed of lime mixed with chromic oxide. The refined metal crystallises in cubes or octahedra and still contains about 1·5 p.c. carbon. By further refining, however, with a double oxide of chromium and calcium, the pure metal is obtained (Moissan, The Electric Furnace).

Pure chromium is a steel-grey metal, slightly harder than glass; the carbides, however, are harder than quartz, so that a metal with between 1·5 and 3 p.c. carbon can only be cut and polished by diamond dust. Its density is 6·92, and it oxidises superficially in moist air; the melting-point is probably above 2000°. The pure finely divided metal burns rapidly when heated in the blowpipe flame, and a pyrophoric powder may be prepared by distillation of chromium amalgam *in vacuô* (*v. infra*). It also unites with nitrogen when heated in nitrogen or ammonia, forming a very stable *nitride*. Crude chromium does not burn until heated to above 2000°. It combines with sulphur vapour at 700°, and when heated to redness in hydrogen chloride, forms *chromous chloride*. Electrolytic chromium occludes 250 times its volume of hydrogen. Aqueous hydrochloric acid acts slowly on the metal, but the action is accelerated if the chromium is made the anode in electrolytic hydrochloric acid. Heating with sulphuric acid causes evolution of sulphur dioxide; concentrated nitric acid and *aqua regia* have no action. As in the case of iron, *active* and *passive* varieties of chromium exist; in general, the metal is rendered passive by oxidising solutions, whilst hydrogen ions make it active. In the electromotive series, the active chromium immediately follows zinc, the inactive metal is near platinum. The cause of the passive state is usually ascribed to the existence of a superficial film of oxide, but this view has been disputed.

Alloys. Various alloys of chromium have been prepared, chiefly by means of the electric furnace, by the 'thermit' method, or by the mixture of the molten metals.

Molten *zinc* dissolves but little chromium; a hard and brittle alloy has been obtained in the form of hexagonal lamellæ. *Aluminium* and chromium mixtures, containing between 5 and 55 p.c. chromium, separate into two liquid layers, and probably contain a compound, Cr_3Al. The alloys with a low percentage of chromium are brittle, one containing 13 p.c. chromium can be powdered in a mortar.

Alloys with *antimony* are brittle, and compounds represented by SbCr and Sb_2Cr are known. Chromium alloys with *copper* with difficulty, but an alloy can be obtained by stirring in copper oxide into a molten alloy of aluminium and chromium (Moissan). The liquid metals are miscible only to a small extent.

Cobalt and chromium are miscible in all proportions, both in the liquid and the solid states, and yield a mixture of minimum melting-point (1320°) with 47 p.c. Cr. Homogeneous alloys, containing above 30 p.c. Cr, when cooled, separate into two sets of crystals, distinguishable by electrolytic etching.

Nickel chromium alloys with less than 90 p.c. nickel are non-magnetic.

Silver and chromium, although partially miscible in the liquid state, form no solid solution. Molten *cadmium* does not dissolve any chromium. Molten mixtures of *lead* and chromium, containing more than 27 p.c. lead, separate into this mixture and pure lead.

Chromium also forms *silicides* and *borides* in the electric furnace; of the former, compounds represented by $SiCr_3$, $SiCr_2$, Si_3Cr_5, and Si_3Cr, have been described. They are very hard—$SiCr_2$ is harder than corundum—and are not attacked by ordinary acids, though attacked readily by hydrofluoric acid and by *aqua regia*. The *borides* Cr_3B_2 and CrB are metallic-looking crystalline solids, not attacked even by a mixture of *aqua regia* and hydrofluoric acid. The compound CrB is stated to be weakly magnetic. The *phosphide* CrP, obtained from the metal and copper phosphide, forms dull-grey crystals, sp.gr. 5·71, which burn in oxygen, forming chromium phosphate, but are unattacked by all acids except a mixture of hydrofluoric acid and *aqua regia*.

By electrolysis of a strongly-acid solution of chromic chloride, using a platinum anode and a mercury cathode, an amalgam Hg_3Cr is obtained, soft and brilliant, and altering but slightly in air. By pressure, a harder amalgam HgCr is obtained, which alters in air more rapidly. By distillation *in vacuô*, both lose mercury and yield pyrophoric chromium (*v. supra*). An amalgam may also be obtained by the action of sodium amalgam on a chromium salt.

With *iron* the alloys of chromium are of great interest. The presence of chromium in iron or steel produces a much finer texture, greater hardness, tenacity, and elasticity, and greater smoothness of fracture. Chromium cannot be used to replace carbon in steel, as has been asserted (Boussingault).

When crystalline, the tendency of these alloys is to produce needles instead of plates, as in the case of manganese. Two to 4 p.c. chromium with 1·2 to 1·4 p.c. carbon, renders it so hard that it is bored with difficulty, and when tempered has a fracture resembling porcelain. In these alloys of steel and chromium, the hardness is probably due to the formation of a definite ferro-chrom-carbide of great hardness, which is completely miscible with its components. All alloys containing between 10 and 90 p.c. chromium appear to consist of two structural elements, that separating primarily being the softer. *Chrome-steel* is now very largely used in railway work for the manufacture of tyres and springs. It also possesses great penetrating power and penetrating resistance, and is therefore largely used for the manufacture of armour plates and armour-piercing projectiles; the addition of nickel further increases its toughness and use in armour plating. Chrome steel is also used in the manufacture of special kinds of files. The alloy is usually prepared of the requisite composition by the addition of a definite amount of 'ferrochrome,' containing from 40 to 85 p.c. chromium to the molten steel. The 'ferrochrome' is prepared from rich chrome-

iron ores in blast furnaces by the use of coke and hot high-pressure blast.

The addition of chromium decreases the magnetic properties, but all alloys, to 80 p.c. chromium, are magnetic. A *carbide* of *chromium* and *tungsten* of great hardness and of sp.gr. 8·41, has been produced in the electric furnace, and to it the special properties of *chrome tungsten steels* are probably due. These latter (as well as *chrome molybdenum steels*), containing up to 3 p.c. chromium and 8 p.c. tungsten, are used for the manufacture of machine tools.

Detection of Chromium. When heated strongly, all compounds of chromium impart a green colour to a borax bead in both the reducing and oxidising flames. On ignition with potassium nitrate, all chromium compounds produce a yellow colour, due to the presence of potassium chromate. If this is dissolved in water, the addition of a solution of lead acetate produces a precipitate of chrome yellow. A similar oxidation occurs when chromium compounds are fused with sodium peroxide, or when solutions of chromium salts are boiled with sodium peroxide.

Solutions of chromic salts or salts of sesquioxide of chromium have an acid reaction. With caustic alkalis they produce a green precipitate of hydrated oxide partially soluble in excess of the reagent, but reprecipitated on boiling the solution. With carbonates, a green precipitate is produced, likewise soluble in excess.

Chromates (in which the chromium exists as an acid) are usually strongly coloured. Soluble chromates are reduced, when warmed with sulphuric acid and a reducing agent such as alcohol, with the production of a green colour. The chromium is then present as a base, and may be precipitated, as already mentioned. When heated with hydrochloric acid, they are partially reduced, with evolution of chlorine and formation of chromium chloride and chloride of the metal present as chromate, together with the formation of *chromyl chloride* CrO_2Cl_2.

Solutions of chromates containing no free acid except acetic acid give a yellow precipitate with a salt of lead, a red precipitate with silver nitrate, and a yellow precipitate with a salt of barium.

Estimation.—When present as a base, chromium is usually estimated as sesquioxide Cr_2O_3. For this purpose, the solution is heated nearly to boiling, ammonia solution added in slight excess, and the temperature maintained until the liquid is perfectly colourless, indicating that the hydroxide, which is slightly soluble in excess of ammonia, is completely precipitated. The precipitate is well washed by decantation and transferred to a filter, washed thoroughly with hot water, dried, and ignited. The oxide produced contains 68·63 p.c. of chromium. The precipitation is not complete in presence of organic matter, and when a glass vessel is used, the precipitate always contains a small percentage of silica. Chromium, when present as a chromate, cannot be estimated directly by that method. It requires to be first reduced to a base. For this purpose, hydrochloric acid and a small quantity of alcohol are added, and the solution heated until the odour of alcohol is dispelled. The chromium may then be precipitated as above. For the direct estimation of chromium in chromates, the precipitation with lead acetate is most satisfactory. The solution is mixed with sodium acetate and acidified strongly with acetic acid. A solution of normal lead acetate is then added, and the precipitate of $PbCrO_4$ is collected on a weighed filter, washed, dried at 100°, and weighed. It contains 16·19 p.c. of chromium, or 31·06 p.c. of chromic anhydride CrO_3. The following scheme may be adopted for the estimation of chromium in chrome iron ore: A few grams of the carefully sampled mineral are ground in an agate mortar and passed through a fine muslin sieve. The dust so produced is further ground in small portions until all grittiness, on passing a little between the fingers, has disappeared and the ore cakes as an impalpable powder round the pestle. About 0·5 gram of the powder is weighed into a platinum crucible of about 50 c.c. capacity, covered with twelve times its weight of recently fused hydrogen potassium sulphate (potassium bisulphate), and gently heated to just fuse the sulphate. After keeping at this temperature for 15 or 20 minutes, the heat is gradually increased until the crucible bottom becomes red hot. The fused mass should not be allowed to rise above half-way up the crucible. The mixture soon fuses quietly, and evolves dense fumes of sulphuric acid; the heat is gradually increased to bright redness. In about half an hour, 6 parts of powdered anhydrous sodium carbonate are added and the mixture again fused for an hour at a red heat, 6 parts of nitre being added in small portions. The temperature is then raised to a full red heat for about 20 minutes; the crucible cooled and transferred to a porcelain basin where the mass is boiled out with water. The solution is filtered, and the residue washed with hot water until the filtrate comes through colourless. The filter and its contents are dried, the precipitate detached and placed with that still remaining in the basin, the filter paper burned, and the ash also added. To ascertain if the fusion has been satisfactory, this residue is digested with moderately strong hydrochloric acid, when the whole should dissolve. Any insoluble black residue indicates either imperfect grinding or insufficient fusion. It must be collected on a filter, dried, and the whole ignited in a crucible and treated with potassium bisulphate, &c., as in the first instance. The aqueous extract, after fusion, is mixed with the main solution. To the liquid, a few grams of ammonium nitrate are added, and the whole evaporated to dryness, taken up with water, and filtered from the alumina, silica, &c., into a porcelain basin. An excess of sulphurous acid solution is then added, and the solution heated until that gas is nearly expelled. The chromate, having thus become reduced to chromium sulphate, a *slight* excess of ammonia is added, and the solution boiled until colourless. The precipitated chromium hydroxide is washed by decantation with hot water, transferred to the filter, and washed with hot water six times. The use of the suction pump is of great assistance in this operation. The precipitate and filter are then dried, transferred to a weighed platinum crucible, and heated gently until the paper is charred. The crucible lid is then placed at the edge of the crucible so that the flame may reverberate into the crucible, and the whole ignited strongly for 10 or 15

minutes. The weighed precipitate should show no yellowish colour on treatment with a few drops of water; if such a colour is produced it indicates imperfect washing of the precipitate from alkali salts. The oxide contains 68·63 p.c. of chromium.

The oxidation may also be effected by means of sodium peroxide, and the chromate produced, instead of being reduced to chromic oxide, may be estimated as chromic acid volumetrically. For this, various methods are available, *e.g.*: (1) boiling with standard arsenious oxide and estimating the excess by standard iodine; (2) adding potassium iodide and titrating iodine liberated by standard thiosulphate; (3) adding standard ferrous ammonium sulphate solution and titrating excess with standard potassium dichromate.

A speedy and accurate method for the estimation of chromium in ferrochrome or chromite, is the following: 1 part of the ore is finely powdered, as described above, and fused with a mixture of 5 parts of sodium peroxide and 8 parts of caustic soda in a silver crucible. The aqueous extract is filtered and again similarly treated; three or four such fusions are necessary to dissolve all the ore, when the only residue is a little silver extracted from the crucible. The filtrate is acidified with sulphuric acid, boiled for 40 minutes and diluted to a known volume. An aliquot part is then titrated with potassium iodide and standard sodium thiosulphate.

Chromates may also be readily estimated in acid solution by hydrazine sulphate, whereby nitrogen is liberated, 100 c.c. of nitrogen at N.T.P. being equivalent to 0·59576 gram Cr.

Compounds of Chromium.

Chromium forms a number of oxides; of these, *chromous oxide* CrO, and *chromic oxide* or *chromium sesquioxide* Cr_2O_3, are definite basic oxides, yielding with acids salts in which chromium is present as a divalent or trivalent cation, forming the *chromous* and the *chromic* salts. Chromic oxide can also combine with bases to form salts, the *chromites*, of the type $MCrO_2$, in which the chromium is present in the monovalent anion CrO'_2. *Chromic anhydride* CrO_3 is an acid anhydride forming, with bases, salts of the type M_2CrO_4, the *chromates*, or $M_2Cr_2O_7$, the *dichromates*, in which the chromium exists as the divalent anion CrO''_4 or $Cr_2O''_7$. Other oxides have been prepared and are usually regarded as compounds of the basic and acid oxides, *e.g.* $Cr_2O_3 \cdot CrO_3$ = *chromic chromate*. The chromous salts are of no industrial importance at present.

Chromic oxide, *Chromium sesquioxide* Cr_2O_3. This compound is produced by the oxidation of metallic chromium and by ignition of chromic hydroxide, chromic anhydride, and certain chromates.

Wöhler prepared this oxide in fine, small rhombohedral crystals by passing the vapour of chromyl dichloride through a tube heated to redness. The crystals are isomorphous with corundum and of equal hardness; their sp.gr. is 5·21. Crystalline chromic oxide is also obtained when a mixture of potassium dichromate and sodium chloride is heated to redness (Ditte, Compt. rend. 134, 336). The finest coloured amorphous chromium oxide is produced by heating mercurous chromate Hg_2CrO_4 in a covered crucible; mercury and oxygen escape, and the oxide remains as a green powder. For the preparation of this substance on the large scale, a great number of methods are recommended.

Boil a solution of potassium dichromate with half its weight of flowers of sulphur so long as the green hydroxide is precipitated. The addition of a little potash solution, by forming potassium sulphide, accelerates the decomposition. The precipitate is filtered from the solution containing potassium sulphate, and washed. The sulphur retained in the precipitate may be removed by heating. Instead of performing the reaction in the wet way, the mixture may be ignited in a crucible, and the resultant mass digested with water (Lassaigne, Ann. Chim. Phys. [3] 14, 299). Wöhler (Pogg. Ann. 10, 46) heats a mixture of potassium dichromate with its own weight of ammonium chloride and a small quantity of sodium carbonate, and purifies the residue by washing.

According to Barian (Rev. Scient. 20, 425), a very pure colour, suitable for colouring fine porcelain, is produced by igniting in a crucible a mixture of 4 parts of potassium chromate and 1 part of starch. The mass is washed free from potassium carbonate and reignited.

Chromic sesquioxide is a green pigment of great permanence. It is not acted upon by chlorine or sulphur gases or by an intense heat. At a white heat it melts, and crystallises on cooling.

Hydrogen and carbon monoxide are without action, but it is reduced to the metallic state on heating with carbon at a temperature of 1185° or higher.

This oxide is largely used under the names *chrome green* (mixtures of *chrome yellow* and Prussian blue are also frequently called *chrome greens* and must not be confounded with the true chrome green), and *ultramarine green* for imparting a green colour to glass, porcelain, &c., as a pigment, in oil and water colours and in printing, and as a mordant in calico-printing and dyeing. Certain hydrated oxides are also used under various names; their colours are, generally speaking, brighter than that of the anhydrous oxide, but they usually contain small quantities of other substances besides the oxide and water.

Guignet's Green; *Pennettier's Green*; *Emerald Green*; *Veridian* $Cr_2O_3,2H_2O$. This pigment appears to be identical with that formerly manufactured in secret by Pennettier. According to Guignet's method, 3 parts of boric acid and 1 part of potassium dichromate are heated to dull redness in a reverberatory furnace. The mass swells up, evolves oxygen, and becomes of a fine green colour; it contains the borates of potassium and chromium, or a double borate of those two metals. It is boiled with water, whereby the borate of chromium is decomposed into boric acid and hydrated chromium sesquioxide, potassium borate also remaining in solution. The precipitate is well washed, dried, and finely ground. It usually contains boric acid even after thorough washing. The washings and mother liquors are evaporated for the recovery of the boric acid.

According to the Chem. Zeit. 9, 851, the process now used on the large scale is as follows: The boric acid is first purified by solution in hot

water, treated with animal charcoal, and recrystallised. The crystals are dried in a centrifugal machine. The mother liquor may be employed three or four times for recrystallisation of fresh portions of acid, but becomes then too impure for further use. Eight parts of potassium dichromate and 3 parts of purified boric acid are ground into a stiff paste with water, and the mixture in charges of about 1 cwt. is heated to dull redness for about 4 hours in a reverberatory furnace. The fused mass is thrown into water, and washed repeatedly by decantation; the pigment is ground while wet, again washed, filtered, and dried. The first two washings contain considerable quantities of potassium borate, which is recovered by evaporating in leaden pans, adding hydrochloric acid and allowing the boric acid formed to crystallise. The mother liquor is further evaporated and crystallised. The crystals are redissolved, the lead (from the pans) precipitated by hydrogen sulphide, and the filtrate recrystallised. In this manner, from 70 to 75 p.c. of the boric acid is recovered.

Guignet's green is the most permanent green pigment known; it is unacted upon by light or concentrated boiling alkalis; it is not affected by acids in the cold, but hot hydrochloric acid slowly dissolves it. When heated to 200° it becomes anhydrous. It is a fine green pigment largely used for the same purposes as the ordinary oxide. It may be used in place of the dangerous arsenical greens. It possesses good covering power, and can be mixed with other pigments without alteration. When mixed with lead chromate, it is employed for the production of a pale-green colour in landscape painting.

Other *chrome greens* are obtained by the use of sodium phosphate. These always contain some phosphoric acid. They are, however, not as brilliant as the oxide chrome greens. Various methods of preparation are employed. Arnaudon dissolves ammonium phosphate with slight excess of potassium dichromate in a little boiling water, evaporates until mass solidifies on cooling, heats at 80° and later at 200°, washes with hot water, dries and powders. Another method consists in boiling a solution of 10 lbs. potassium dichromate with 18 lbs. sodium phosphate, adding 10 lbs. sodium thiosulphate and a little hydrochloric acid, and boiling until precipitation is complete. The precipitate is washed, ground, and dried.

According to Bong (Ber. 29, 201), a blue pigment, retaining its colour at high temperatures, suitable for colouring porcelain, &c., is produced by igniting strongly, in the air, an intimate mixture of 5 parts boric acid, 15 parts alumina, 20 parts magnesium carbonate, and 2 parts barium chromate.

Chromic chloride or $CrCl_3$ or Cr_2Cl_6. The anhydrous chloride is obtained by heating a mixture of carbon and chromium sesquioxide in a current of chlorine. It forms pale-violet scales of sp.gr. 3·03; it is almost insoluble in water, but dissolves readily, being transformed to the green variety (*v. infra*), if only a minute trace of chromous chloride (1 in 20,000) is present. Chromic chloride may be prepared in solution by dissolving the hydroxide in hydrochloric acid. It forms two isomorphous hexahydrated salts ($CrCl_3,6H_2O$), one blue and the other green, and also a tetrahydrate and a decahydrate. The blue hexahydrate, when dissolved in water, appears to give the ions $Cr(OH_2)'''_6$ and $3Cl'$, all the chlorine being precipitated by silver nitrate; the green salt, however, at first forms the ions $Cr(OH_2)_4Cl_2,2H_2O$ and Cl', only $\frac{1}{3}$ its chlorine being immediately precipitated (Werner and Gubser, Ber. 1901, 34, 1579). In calico-printing, a neutral solution of chromic chloride, prepared from potassium dichromate, is frequently used. The following method is recommended by De Karrur: Dissolve 9 lbs. of potassium dichromate in 5 gallons of boiling water. Prepare also a solution of 9 to 11 lbs. of white arsenic in 24 gallons of boiling water, and mix, with constant stirring, with the solution of dichromate. A greenish precipitate of chromic hydroxide soon separates; it is cooled, filtered, and washed with boiling water. The precipitate is added in portions to a solution of hydrochloric acid (diluted until it no longer fumes), with constant stirring, until a portion remains undissolved. A solution of soda is then added and well mixed, until the hydroxide begins to precipitate. The dark-green solution, being thus neutralised, is evaporated to 46°B. and is ready for use. A basic chloride $CrCl(OH)_2$ is also employed as a mordant for silk and cotton.

Chromic fluoride $CrF_3,4H_2O$. This product is used in the printing and dyeing of woollen goods. It is a fine crystalline green powder, very soluble in water. It has a corroding action on glass, and is therefore best kept in lead or wooden vessels. It may be used as a mordant with both vegetable and animal fabrics, and is often employed in the place of acetate or nitrate of chromium for printing, and in general gives finer results. Alizarin dyes, cœruleïn, galleïn, &c., and logwood extracts, are fixed as perfectly as with acetate of chromium. One advantage in using it is that it is solid. It has no injurious effect on the pile, and is often used in place of chromates where the oxidising action of these is injurious, especially with wools. *Chromium silicofluoride*, prepared by dissolving the oxide in hydrofluosilicic acid, has also been used in dyeing and printing in place of the fluoride, and is stated to give better results.

Chromium sulphates. These are prepared by the dissolution of the hydroxide in sulphuric acid. It yields a bluish-violet solution, which, on boiling, becomes green. The experiments of Recoura have shown that numbers of compounds of different constitution exist both in the violet and green varieties, but they are not of commercial interest. The double sulphates of chromium and potassium, sodium and ammonium, are, however, of importance. These are known as *chrome alums*; they crystallise in fine octahedral crystals containing 24 molecules of water isomorphous with those of ordinary alum, and of corresponding composition.

Potassium chrome alum, *Chrome alum*

$$Cr_2(SO_4)_3{\cdot}K_2SO_4,24H_2O.$$

This substance may be prepared by mixing solutions of chromic sulphate and potassium sulphate in molecular proportions, or more conveniently by the reduction of potassium dichromate in sulphuric acid solution.

The best method is to add 5 parts of strong sulphuric acid to a solution of 3 parts potassium dichromate in 30 parts of water with the addition

of a reducing agent, preferably a current of sulphur dioxide:

$$K_2Cr_2O_7+H_2SO_4+3SO_2+24H_2O = K_2SO_4\cdot Cr_2(SO_4)_3,24H_2O+H_2O.$$

When the sulphur dioxide is substituted by other reducing agents, such as alcohol, a larger quantity of sulphuric acid is required.

Chrome alum is obtained in large quantities as a by-product from the oxidation of organic substances by a mixture of potassium dichromate and sulphuric acid, as in the oxidation of anthracene to alizarin, in the manufacture of aniline violet, &c.

It crystallises in fine dark-purple octahedra, especially in presence of excess of acid, is soluble in 7 parts of cold water, forming a reddish-blue solution, which, when heated to about 70°, becomes green. It returns to its original colour after standing some weeks.

When heated to 25°–30°, the crystals lose half their water and become lilac-coloured; at 100° a further quantity of water escapes and the crystals turn green; at 350° they become anhydrous, but are still soluble in water; at a temperature slightly above 350° they become greenish-yellow, insoluble in water (Löwe), and only slowly soluble in acids. The green salt only contains ⅓ of the SO_4 as an acid ion, and is probably a sulphate of a sulphochromyl hydroxide. For these compounds, reference should be made to the extensive researches of Recoura (Ann. Chim. Phys. [7], 4, 494).

Chrome alum is used in dyeing, calico printing, and tanning.

Sodium chrome alum $Na_2SO_4\cdot Cr_2(SO_4)_3,24H_2O$ corresponds to the potassium salt, but is more soluble in water.

Ammonium chrome alum

$$(NH_4)_2SO_4\cdot Cr_2(SO_4)_3,24H_2O$$

is prepared like the preceding alums. It is less soluble in water than potassium chrome alum. It melts at 100°.

Chromium chlorate $Cr_2(ClO_3)_6$ is used to some extent in calico printing (Despierres and others, Dingl. poly. J. 228, 260–263), and for increasing the permanence of aniline black. It may be prepared by the addition of a solution of potassium chlorate to chrome alum or by the addition of barium chlorate to a solution of chromium sulphate, the barium sulphate being precipitated. According to Lauber and Weinreb (Dingl. poly. J. 257, 290), it is best prepared by the following process: Dissolve 60 parts of chrome alum in 80 parts (by weight) of hot water; add 20 parts of soda dissolved in 60 parts of water, and wash the precipitated hydroxide. Redissolve the precipitate in 10 parts of cold sulphuric acid of 66°B., filter if necessary and add 22 parts of potassium chlorate dissolved in 50 parts of water. The solution is evaporated slightly and the potassium sulphate crystallised out; the more soluble chromium chlorate remains in solution. When heated at 100° it gives off quantities of chlorine and forms a yellow-red liquid containing chromic acid and other compounds.

Chromic anhydride, *Chromic acid* CrO_3. This important oxide is best prepared by the decomposition of a chromate by sulphuric acid. A cold saturated solution of potassium chromate is added to from 1 to 1½ parts of concentrated sulphuric acid, with constant stirring. On cooling, if the acid used be strong enough, crimson crystals of chromic anhydride separate; if necessary, the solution is evaporated until the crystals are formed on cooling. The liquid is poured off and the crystals drained on porous tiles or pressed between porous plates. They may be recrystallised by dissolving in water and evaporating to a syrup. The excess of sulphuric acid may be removed by the cautious addition of barium chromate to the solution of the crystals, or the crystals may be gently fused, when the heavier oxide sinks to the bottom of the vessel and the sulphuric acid above slowly evaporates. The mother liquors from the chromic anhydride are used for a fresh preparation until the percentage of potassium sulphate becomes excessive; they are then precipitated by the addition of lead acetate with the production of a light-coloured 'chrome yellow' containing much lead sulphate.

According to Zettnow (Pogg. Ann. 143, 468), the largest yield is obtained as follows: 300 grams of potassium dichromate are dissolved in 500 c.c. of water, and 400 c.c. of strong sulphuric acid are added. The mixture is allowed to stand for 10 or 12 hours, the solution decanted from the deposited crystals of potassium sulphate, and heated to 80° or 90°; 150 c.c. of sulphuric acid are then added, followed by sufficient water to redissolve the chromic anhydride at first deposited, and the solution evaporated until the oxide commences to crystallise. The mixture is allowed to stand for 12 hours, decanted from the crystals, and evaporated with the production of a second and third crop of crystals. The crystals are drained, introduced into a crucible, mixed thoroughly with 50 c.c. of nitric acid of not less than 1·46 sp.gr. (weaker acid would dissolve the crystals) and drained for some hours on a tile. The operation is repeated if necessary with 25 c.c. of nitric acid. The whole of the sulphuric acid and sulphate having been thus removed, the crystals are heated on a sand-bath and the nitric acid evaporated, or they may be heated to 80° in a current of air. In this manner, Zettnow obtained from 85 to 90 p.c. of the theoretical yield of pure dry chromic anhydride.

Duvilliers (Compt. rend. 75, 711) prepares this oxide by dissolving 100 parts of barium chromate in 100 parts of water and 140 parts of nitric acid of sp.gr. 1·38 (40°B.) and heating the solution until it becomes red. 200 parts of water are then added, and the whole boiled for 10 minutes; cooled, and the barium nitrate allowed to crystallise out. The solution is decanted, evaporated to the bulk occupied by the original amount of acid used, and a further crop of crystals of barium nitrate removed. The solution, which contains only about 1 part of barium nitrate for 200 parts of the anhydride, is evaporated nearly to dryness, a little water added, and the evaporation repeated until all the nitric acid is driven off. The anhydride is then crystallised out and dried as usual.

Barium chromate is digested for some time with about half the amount of dilute sulphuric acid required for complete precipitation, with the production of chromic anhydride and barium dichromate and precipitation of barium sulphate. Sufficient sulphuric acid is then added to just precipitate the barium, and the solution, which only contains chromic anhydride, is

decanted from the precipitate and the solution evaporated (Meissner). According to C. Watts, the barium chromate is best treated with excess of strong nitric acid, the precipitated chromic oxide filtered through asbestos, and the nitric acid driven off by heat.

Chromic anhydride is a powerfully acid substance crystallising in scarlet rhombic prismatic needles of sp.gr. 2·788 (Zettnow). They melt at 193° without decomposition, and the melted mass exhibits supercooling; at higher temperatures oxygen is evolved together with red vapours, probably CrO_3.

When heated to 250° they decompose into chromium chromate $CrO_3{\cdot}Cr_2O_3$ with evolution of oxygen. Above that temperature, the whole is converted into chromium sesquioxide. The perfectly dry anhydride, when heated to 120° *in vacuô*, slowly volatilises and condenses in red needles (Arctowski). By the action of light on a solution of this oxide, oxygen is evolved and chromium chromate precipitated as a brown powder.

Chromic anhydride is very soluble in water. 100 parts of water, at 26°, dissolve 62 parts of the oxide. The aqueous solution contains Cr_2O_7'' ions, with a small proportion of CrO_4' ions. These ions are capable of transformation by the action of acids or alkalis, as indicated by the equations:

$$(1)\quad Cr_2O_7'' + 2HO' \rightleftarrows 2CrO_4'' + H_2O.$$

$$(2)\quad 2CrO_4'' + 2H \rightleftarrows Cr_2O_7'' + H_2O.$$

It dissolves in acetic acid or ether without decomposition; is almost insoluble in sulphuric acid of 1·77 sp.gr., but dissolves in stronger or weaker acid; is insoluble in nitric acid of sp.gr. 1·46.

Chromic anhydride is a powerful oxidising agent. Warm anhydrous alcohol inflames when dropped upon it, and even dry ammonia gas is oxidised with production of water and nitrogen. Addition of oxalic acid is said to increase its oxidising power. The solution in water, sulphuric acid, or acetic acid, is largely used as an oxidising agent in organic work. In most of these oxidations, precautions must be taken to moderate the velocity of the reaction. When acetic acid is used as the solvent, the substance to be oxidised is usually dissolved in the same solvent and the oxidising solution slowly added, the temperature being kept sufficiently low, *i.e.* seldom above 100°. Chromic acid, as an oxidising agent, has the advantage that the close of the reaction is frequently indicated by a pure green colour in place of the brownish colour.

It has the property of producing a permanent yellow colour with silk or wool, but not with cotton. The chromium in such material may be converted into lead chromate upon the fibre or further dyed by logwood, &c. Chromic anhydride usually contains sulphuric acid and sulphates or nitrates; Moissan found 24 p.c. of sulphuric acid in samples of the commercial article.

Chromates. *Chrome iron ore.* All chromates are prepared, directly or indirectly, by the action of oxidising agents upon *chrome iron ore* or *chromite* $FeO{\cdot}Cr_2O_3$. This important mineral is found in a large number of localities, principally in Turkey, Greece, Asia Minor, Siberia, and New South Wales. Large deposits of iron ore are found in New Caledonia, containing sometimes 5 p.c. of chromium sesquioxide in a form soluble in acid, probably as chrome ochre.

Chromite belongs to the spinel group of minerals. It is isomorphous with magnetic iron ore $FeO{\cdot}Fe_2O_3$, and may be considered as that substance in which the sesquioxide of iron is replaced by sesquioxide of chromium. A portion of the chromium is usually replaced by aluminium, and some of the iron by magnesium, though this is sometimes absent. The composition of chromite varies extremely; an ore, containing 50 p.c. of the sesquioxide, is of very good quality. Of seven samples from varying localities analysed by Clouet, the chromium sesquioxide present averaged 44 p.c. For analyses *v.* CHROMITE.

Chromite is black or brownish-black, and infusible before the blowpipe. It will scratch glass, but is itself scratched by a good steel knife.

A scheme for the analysis of chromite has been given under the estimation of chromium.

Potassium chromates. Both the normal and acid chromates are of importance in the arts. The acid or dichromate, containing the larger proportions of the active constituent CrO_3, is generally prepared on the large scale.

A great number of processes have been adopted for the treatment of chromite for this purpose; they all depend upon the oxidation of the chromium sesquioxide into chromic anhydride.

The ore is heated to redness and plunged into cold water to facilitate the powdering, stamped, ground in a mill, and finely sifted.

In former times, the ore was mixed with about two-fifths of its weight of potassium nitrate and ignited on the bed of a reverberatory furnace, the oxygen required for the oxidation of the sesquioxide into the anhydride and the potassium for its conversion into potassium chromate, being both provided by the nitrate. A great saving was introduced by the substitution of atmospheric oxygen as the oxidising agent in place of the nitre, the potassium being supplied by potassium carbonate or, as proposed by Watt, by potassium sulphate. The latter salt is largely used where, as in Russia, the demand for potassium sulphate is small, and hence this salt, produced during the later conversion of the chromate to dichromate, is used to replace some of the potassium carbonate. The mass, however, was very liable to fuse and the heavy particles of chromate to sink through the liquid and escape the action of the blast. This difficulty was overcome by Stromeyer, who introduced lime into the mixture, thus rendering the mass porous and non-fusible and much increasing the rapidity and completeness of the action.

Tilghmann (Patent 1847) makes use of felspar as the source of alkali. For this purpose, 1 part of chrome ore is mixed with 4 parts of felspar and 4 parts of lime or 7 parts of chalk. The mixture is heated to bright redness, but not to fusion, in a reverberatory furnace for about 20 hours, with constant stirring. The chromate thus produced is removed as described later.

The ore may also be mixed with potassium chloride, and heated to whiteness with frequent stirring while a current of superheated steam is passed over the mass; the iron is stated to pass away almost entirely as chloride (Swindells, Chem. Gazz. 1851, 419).

Jacquelain (Ann. Chim. Phys. [3] 21, 478) prefers to produce calcium chromate in the furnace and to convert it subsequently into the required chromate by double decomposition. He thus avoids the loss of alkali always experienced in the ordinary process. The ore is *finely powdered*, preferably levigated and dried before use, mixed ultimately with chalk in the required proportions, and heated to bright redness on the bed of a reverberatory furnace for 9 or 10 hours, with occasional stirring (at least once an hour). The product is ground in a mill, suspended in hot water, and treated with sulphuric acid until slightly acid; calcium dichromate is thus produced. A little chalk is stirred into the solution to precipitate the iron as oxide, and a solution of potassium carbonate or other salt, according to the chromate required, is added. The calcium is thus precipitated as carbonate and the dichromate required remains in solution. The solution may also be used directly for the production of chrome yellow, &c.

According to Booth's method (Pat. 1852, Dingl. poly. J. 131, 137), the ore is mixed with one-fifth of its weight of charcoal or coal and ignited in a reverberatory furnace like that used for puddling iron, out of contact with the air. The product is thrown into vats, and the reduced iron dissolved out by dilute sulphuric acid, the residue being treated in the usual manner for the production of chromates. The weight of oil of vitriol used, amounts to about two-thirds that of the ore. It is stated that the value of the ferrous sulphate obtained repays the extra labour involved.

Atcherley (Hoffman's Ber. u. Entw. Chem. Ind. [1] 725) gives a description of the manufacture of potassium dichromate as usually practised on the large scale, of which the following is the abstract:—

The ore is stamped, ground in a mill, and passed through a sieve of 80 meshes to the inch.

Potash lye is prepared by soaking 7 cwts. of burned limestone (containing but little silica and magnesia) in a solution of 2¼ p.c. of potassium carbonate free from chloride (which would hinder the crystallisation of the product), dried, ignited, and powdered.

It is then mixed with 4½ cwts. of the ore, and spread in a layer 2 inches deep upon the previously heated bed of a reverberatory furnace, at the end nearest the fire. The furnace is about 9 feet long and 6 feet broad. The heat is maintained at bright redness, and the mixture turned over every 15 minutes; in about 2 hours it is gradually pushed towards the farther end of the furnace, and its place supplied by a fresh charge. The operation is completed in about 4 hours, when the mass is greenish-yellow and contains chromates of potassium and calcium, lime, potassium silicate, and ferric oxide. It is broken into coarse powder and lixiviated in wooden pans, placed steplike one above another, with a hot solution of potassium sulphate, which converts the calcium chromate into potassium chromate with precipitation of calcium sulphate. The liquid is allowed to run from one vat to another, until at last a saturated solution of potassium chromate is produced. This is run into a depositing vat lined with lead and treated with sufficient sulphuric acid and water to convert the normal salt into the dichromate, and the solution cooled.

As the solution of normal chromate was saturated and contained about 1 part of salt in 2 parts of solution, the dichromate solution formed is supersaturated, that salt requiring nearly five times as much water for solution as the normal chromate; about three-quarters of the total amount in solution is thus deposited on cooling. The crystals are redissolved in sufficient water to form a solution of 1·120 sp.gr. and crystallised in deep iron pans at a temperature of 21°.

The production of chromates is said to be rendered easier by the addition of oxygen-carriers, such as manganates or oxides of copper or iron (D. R. P. 163814). A method dependent on this, in which ferric oxide obtained by heating pyrites is used, is the following: 240 parts chrome iron ore of 50 p.c., 170 parts sodium carbonate, and 150 parts ferric oxide, with, if desired, 50 to 80 parts lime, are intimately mixed, roasted, and lixiviated. The residue contains all the original ferric oxide and may be used over again. The solution is concentrated and treated as usual. The action of the ferric oxide is regarded as due to the production of an alkaline ferrite which becomes converted to the chromate and ferric oxide (J. Soc. Chem. Ind. 1895, 865).

Chromates are also produced by mixing finely divided chrome iron ore with alkaline carbonates and roasting in an oxidising atmosphere in a revolving furnace at a temperature sufficient to keep the mass fluid (National Electrolytic Co. New York; J. Soc. Chem. Ind. 1908).

Potassium chromate K_2CrO_4 is prepared, as already described, from chrome ore. It may be produced by adding potassium hydroxide to a solution of the dichromate. It crystallises in anhydrous yellow rhombic prisms isomorphous with those of potassium sulphate, sp.gr. 2·71 (Kopp). 100 parts of water dissolve of potassium chromate

at	0°	30°	60°	105·8°
	54·57	65·13	74·6	88·8 parts,

105·8° being the boiling-point of the saturated solution. The solution has a fine yellow colour of great tinctorial power; a distinct yellow tinge is imparted by 1 part in 400,000 parts of water. It is insoluble in alcohol and ether, and is very poisonous, producing a condition resembling diabetes when administered by mouth or subcutaneously. It also produces slow-healing sores, especially among workers in chromate factories. For these, a sodium bisulphite wash is efficacious. Such workers should pay attention to constant washing of face, nose, and hands, and packers are advised to wear respirators.

When heated, it reddens and fuses without decomposition; heated with reducing agents, such as sulphur, it is reduced to chromium sesquioxide. The addition of an acid, even carbonic acid, determines the decomposition into potassium dichromate, as is indicated in the previous equations, and it is evident further that, even when excess of acid is present, the solution still contains CrO_4'' ions. The equations also indicate that a solution of potassium chromate possesses an alkaline reaction

$$2CrO_4'' + H_2O \rightleftharpoons Cr_2O_7'' + 2HO'.$$

Owing to the much smaller solubility of the dichromate (4·64 parts at 0°), when the chromate is crystallised some dichromate also separates.

Potassium chromate is not largely used, the dichromate, on account of its greater richness in chromic acid, being generally preferred. The general uses and oxidising properties, however, described under potassium dichromate, also apply to the normal chromate.

Potassium dichromate, generally known as 'Bichromate,' or 'Bichrome,' $K_2Cr_2O_7$. This important salt is prepared in large quantities by the methods already described. It may be made electrolytically by the use of a solution of potassium hydroxide, a cathode of porous copper oxide, and an anode of ferrochrome (50 p.c.), which has an E.M.F. of 2 volts: ferric oxide is also formed and precipitated (Lorenz, Zeitsch. anorg. Chem. 1896, 12, 396). Considerably over 10,000 tons are annually produced in Great Britain.

It crystallises in anhydrous, fine, red, square tables, derived from triclinic prisms, of sp.gr. 2·692, and of intensely metallic, bitter taste. They melt at about 400° (Tilden and Shenstone), and resolidify on cooling without change. At bright redness, decomposition ensues, and the normal chromate and chromic sesquioxide result. Other chromates of composition, $K_2Cr_3O_{10}$ and $K_2Cr_4O_{13}$, appear to exist in equilibrium with the solution with certain limits of concentration.

100 parts of water dissolve at 0°, 4·64 parts; at 30°, 18·13 parts; at 60°, 45·44 parts; and at 104·8°, 108·2 parts; 104·8° being the boiling-point of the saturated solution (Koppel and Blumenthal, *l.c.*).

Potassium dichromate is used in the preparation of all chrome pigments; of 'discharge' for Turkey red, &c.; for the production of a large variety of colours in calico printing and dyeing; in the manufacture of safety matches, &c. In solution with sulphuric acid, it is used as a bleaching agent for tallow, palm oil, &c.; in the oxidation of anthracene to alizarin, and in the manufacture of aniline violet and in many other organic oxidations. It is also used for tanning leather (*v.* LEATHER).

When mixed with organic substances it is reduced on exposure to light; gelatin under such circumstances is rendered insoluble. This reaction is taken advantage of in the 'Carbon' process of photography. The gelatine is mixed with a pigment of any colour, and the paper carrying this film is sensitised by floating on a solution of potassium dichromate. On exposure under a negative, the gelatine in those portions exposed to the light becomes insoluble, and retains the pigment, while the portions protected by the darker parts of the negative are almost unacted upon, and may be dissolved in warm water. In this manner, photographs of any desired colour, and of great beauty and permanence, may be produced. Contact of the chromated gelatine with the reduced silver of an ordinary bromide print has a similar effect, and bromide photographs may hence be copied by squeezing into contact with a sentitised pigmented gelatine. After a few minutes' contact, the pigmented paper is developed like a carbon print. The bromide has become bleached and reduced to silver, but can be redeveloped. The insoluble gelatine does not absorb water, but will take oil, which may be mixed with any desired pigment, and this forms the basis of the *oil* and *bromoil* processes. Gum, mixed with dichromate, is also made insoluble by exposure to light, and this is made use of in photography in the *gum dichromate* process (*v.* PHOTOGRAPHY).

Sodium chromates. The normal chromate $Na_2CrO_4,10H_2O$ and the dichromate $Na_2Cr_2O_7$, $2H_2O$ are prepared by methods corresponding to those used for the potassium salts. According to Nic. Walberg (Dingl. poly. J. 259, 188), they are prepared on the large scale as follows: 6 parts of powdered chrome ore (44 p.c. Cr_2O_3) are mixed with 3 parts soda ash (92 p.c. Na_2CO_3) and 3 parts of chalk, and heated in charges of 1 ton in a reverberatory furnace for 8 hours. The mass is lixiviated to produce a solution of 45°B., boiled down to 52°B., and allowed to crystallise in leaden pans. The crystals are first dried by a centrifugal machine, and finally heated to 30° in a drying chamber, where they crumble to a yellow anhydrous powder containing about 96 p.c. of the normal chromate.

For the production of dichromate, these crystals are dissolved to a solution of 40°B. and treated with sufficient chamber acid to determine the conversion into the dichromate, the right point being found by potassium iodide and starch paper. Sufficient neutral sodium chromate is then added to bring the percentage of CrO_3 to about 72·5. The liquor is cooled in lead tanks to 1°, artificially if necessary, and the sodium sulphate crystallised out. The liquor is drained off, filtered if necessary, and evaporated to dryness in an iron pot, with constant stirring. The residue is powdered while still hot. If the amount of CrO_3 be allowed to exceed 72·5 p.c., the product is damp and cannot be stored in wooden casks. An analysis of this substance showed CrO_3, 72·3; Na_2O, 26·20; SO_3, 1·40.

Normal sodium chromate forms fine large efflorescent crystals of the composition

$$Na_2CrO_4,10H_2O,$$

isomorphous with Glauber's salt. Unlike potassium chromate, it is less soluble than the dichromate; it is, however, more soluble than potassium chromate, 100 parts of water at 30° dissolving 87·36 parts of sodium chromate.

Sodium dichromate $Na_2Cr_2O_7,2H_2O$ crystallises in thin, six-sided prisms with bevelled edges of a fine hyacinth-red colour, and is very soluble in water, 100 parts of water at 30° dissolving 197·6 parts of the salt. It is hence more than 10 times as soluble as potassium dichromate, which frequently makes its use preferable to that of the potassium salt.

Ammonium chromate and **dichromate** are prepared by mixing in proper proportions solutions of ammonia and of chromic acid. The dichromate, on heating, yields nitrogen, water, and chromic oxide, and forms a convenient method for the preparation of nitrogen free from argon.

Lead chromates. The *neutral lead chromate* $PbCrO_4$ is best produced by the action of a solution of lead acetate on a solution of a chromate. Thus produced, it is of a fine lemon-yellow colour, insoluble in water and dilute acids. When heated at 250°, it becomes a reddish-brown, at a higher temperature it fuses, and finally evolves oxygen with the formation of

chromic sesquioxide and a basic lead chromate. On account of this evolution of oxygen on heating, this substance is frequently used in organic analysis.

Lead chromate is soluble in cold lime water or caustic alkali, but is unattacked by hot lime water. For this reason, in immersing calico coloured with chrome yellow in lime water, for the production of an orange colour, care should be taken that the solution is hot.

When heated with caustic alkali, a portion of the chromic oxide is removed, with the production of a basic lead chromate of colour varying from orange to vermilion.

The *normal chromate* is largely used as a pigment, and for calico printing, and is the essential constituent of various chrome pigments as *Chrome yellow, Paris yellow, Leipsic yellow.* The name *Cologne yellow* was originally given to chrome yellow containing a mixture of lead chromate and lead sulphate, but the latter compound is usually present in pale yellows known commercially as 'pure' chrome yellows.

Chrome yellows. The finest chrome yellow is produced by precipitation; the lead acetate used should not be basic, or the product will be of an orange colour; the solution should be dilute, and the lead salt should be in excess; the presence of excess of chromate is liable to 'turn' the yellow—*i.e.* to produce an orange tinge. The substances used should be comparatively pure.

For the lighter yellows, the solution of chromate is mixed with an appropriate quantity of sulphuric acid, Glauber's salts or alum (American chrome yellow), before precipitation; the latter yields good colours but considerable care is required in the precipitation. The lead chromate is thus precipitated, together with any desired amount of sulphate, and the colour correspondingly lowered. For cheaper chromes, the colour is toned down by the admixture of kaolin, barytes, gypsum or whiting, the finely powdered solid being ground with water and well mixed with water in the tank into which the precipitating liquids are run (*vide infra*). Bouthron Chatard gives the composition of ordinary Cologne yellow as $CaSO_4$, 60 p.c.; $PbSO_4$, 15 p.c.; $PbCrO_4$, 25 p.c.

Biot and Delisse first precipitate lead sulphate from a solution of the acetate, and digest 3 parts of the washed precipitate with 1 part of normal potassium chromate dissolved in hot water. The chromate is thus wholly converted into chrome yellow, mixed or perhaps combined with the lead sulphate, and a 'Cologne yellow' of good colour is produced. The colour is said to be equal to that obtained when double the quantity of chromate has been used. Its covering power is, however, stated to be inferior to that of the precipitated yellow.

Liebig uses for this purpose the lead sulphate obtained in dye works, &c., as a by-product. The pigment, on account of the basic character of the sulphate, is of an orange colour.

Anthon substitutes lead chloride for sulphate, treating 100 parts of freshly precipitated chloride with 27 parts of dichromate.

The method usually adopted for production of chrome yellow is the following: The two precipitating solutions are placed separately in wooden tanks, and heated by steam pipes. The solutions are either filtered or allowed to settle in the tanks and drawn off from above. They are run together into the precipitating tank, which contains about 200 gallons. The chrome yellow is allowed to settle and the clear liquid drawn off; more water is added, the whole thoroughly stirred and the process is repeated three or four times. The pigment is then put in a filter press and dried at as low a temperature as possible.

According to the Textile Colourist, the preparation of chrome yellow is as follows: For the preparation of the lead acetate, four wooden tubs, 3 feet in diameter and 1½ feet high, are arranged one above another, so that the liquid may pass downwards from one to the other. They are filled with granulated lead, and strong wood vinegar poured on the uppermost; after remaining there for a few minutes, it is run into the second, third, and fourth for an equal time. The surface of the lead is thus thoroughly acted upon, and becomes heated and oxidised by the air. The vinegar is then passed through a second time, remaining in each tub for an hour; on leaving the fourth tub, a saturated solution of acetate is produced.

Bichrome is dissolved in 10 or 12 parts of water in steam-cased copper pans, and sufficient acetate added to just precipitate the chromate completely. The precipitate is settled, washed by decantation, filtered, and dried slowly on boards. The filtration should be performed as rapidly as possible, because the pigment swells considerably while drying, and this should take place on the boards.

By mixing some lead chromate with the lead acetate solution, a dark lemon colour is produced, and by the addition of caustic potash to the precipitate, a much redder pigment may be obtained.

The chrome yellows, by mixture with Prussian blue, form greens known as 'Brunswick greens' and also as 'chrome greens' (not the true *chrome green, vide supra*). These are valuable and cheap pigments, but not as stable as the corresponding *zinc greens* (*vide infra*).

By removal of some of the acid from normal lead chromate, a *basic* lead chromate of a deep red colour is obtained, $PbO{\cdot}PbCrO_4$, which is the base of a number of *chrome reds.* Between these and the various yellows a large number of shades of *chrome orange* may be obtained. The chrome reds are known by a variety of names, *e.g. Austrian cinnabar, Persian red, Chinese red, Victoria red, Derby red, American vermilion,* &c.

The pigment is usually prepared by boiling chrome yellow with caustic alkali or by boiling together the lead salt, potassium dichromate, and an alkali. One such method is—20 parts of white lead are mixed into a fine paste with water, 10 parts of potassium dichromate and 3 of caustic soda, are dissolved in a little water, added, and the whole boiled until the desired colour is obtained. It is then washed and dried.

Runge mixes 45 parts of litharge, 6 parts of salt, and 50 parts of water; the mass becomes white, and swells considerably; more water is added to prevent it from hardening. In three or four days, the whole has been converted into lead oxychloride; a solution of 15 parts of potassium dichromate is then poured on, and the

mass well stirred and washed. A corresponding process is used with carbonate of lead, the colour produced being preferable to that when chloride, sulphate, or oxide of lead are used.

For the production of a fine ' Persian red,' Prinvolt digests 25 parts of lead carbonate in a cold solution of 10 parts of potassium chromate for 2 days. A red crystalline precipitate of basic lead chromate is thus produced, while potassium bicarbonate remains in solution. The mixture is boiled for half an hour, whereby a portion of the red precipitate becomes decomposed, with the formation of normal lead chromate and of potassium chromate, turning a violet-red colour. This is filtered off, washed, and digested with one part of sulphuric acid dissolved in 100 parts of water, with the production of ' Persian red.'

For the production of a fine vermilion pigment, Liebig and Wöhler's method may be used. A mixture of equal parts of potassium and sodium nitrates is just heated to fusion, and chrome yellow, in small fragments, is dropped in; ebullition takes place, and the mass becomes black. The heating should be continued until ebullition ceases. The chrome yellow has thus become converted into basic lead chromate and potassium chromate. If the temperature used be too high, the product becomes brown and is spoiled. The supernatant yellow liquid is poured from the heavy basic lead salt, which is then well washed in water. The washings should be poured off as quickly as possible, or the action is liable to be reversed and the normal chromate reproduced in part, with a corresponding reduction of colour.

The colour of the varieties of chrome red is due principally to the size of the crystals, those pigments of which the crystals are largest being of the most intense colour.

For the production of *chrome orange*, the chrome yellow is boiled with lime or alkali (in smaller quantity than that used for production of chrome red), until the shade required results. The cheaper chrome orange pigments, as in the case of the yellows, contain admixed kaolin, gypsum, &c.

The lead chromates all possess good covering power and brightness of colour; they are durable, but blacken under the action of sulphuretted hydrogen. They mix well with other pigments, but should not be used with sulphides.

Calcium chromate $CaCrO_4,4H_2O$ is largely produced in the manufacture of chromates from chrome iron ore. It is soluble in water and alcohol. It becomes anhydrous at 200°, and is then almost insoluble in water.

Barium chromate $BaCrO_4$ is a canary-yellow powder, known as *Yellow ultramarine* or *Lemon yellow*. It is produced by the addition of a chromate to a solution of a salt of barium.

Barium chromate is insoluble in water and acetic acid, soluble in hydrochloric and nitric acids. On treatment with a boiling solution of chromium anhydride, it dissolves, and crystallises on cooling as a yellowish-red powder, consisting of the dichromate $BaCr_2O_7,2H_2O$.

Both barium and calcium chromates have been employed as pigments, but are now little used on account of their lack of brightness and covering power.

Bismuth chromates. The addition of potassium dichromate to a neutral solution of bismuth nitrate gives a yellow flocculent precipitate, $3Bi_2O_3{\cdot}2CrO_3$, soluble in acids (Löwe). On heating, it becomes partly decomposed and turns greenish. From an *acid* solution of bismuth nitrate, the precipitate formed consists of $Bi_2O_3{\cdot}2CrO_3$ (Löwe; Muir), and is quite insoluble in water. Bismuth chromate is used as a pigment and in calico printing.

Zinc chromate, Zinc yellow, or Buttercup yellow $ZnCrO_4$, is a beautiful, stable, yellow pigment, produced by the addition of hot neutral solution of zinc sulphate to potassium chromate, or by adding a cream of zinc oxide in water to a boiling solution of potassium dichromate.

Zinc chromate can be obtained in various tints and has a good colour. Though not equal to *chrome yellow* in covering power or body, it has the advantage of not blackening by exposure to sulphides. It is largely used for mixing with *Prussian blue* to form the *zinc greens*, which are more stable and faster to light than the corresponding *chrome greens*.

CHROMOCYANINES *v.* OXAZINE COLOURING MATTERS.

CHROMOMETERS *v.* COLORIMETERS.

CHROMOPHORES and CHROMOGENS. The introduction of artificial dyestuffs of known constitution in the latter part of last century, drew attention to the question whether any relationship could be found connecting the colour of organic substances with their molecular structure. At the time, little information could be derived from a study of the natural dyestuffs in general use (*e.g.* indigo, alizarin, cochineal, &c.), since their constitution was unknown: the study of synthetic compounds promised results, and in 1876 an attempt was made by Otto Witt (Ber. 9, 522) to correlate colour and constitution.

These early endeavours were chiefly directed to finding an immediate relationship between structure and colour rather than to the general question of absorption spectra; in recent years a different standpoint has been adopted, and in studying absorption the invisible portion of the spectrum has been taken into consideration.

A substance is coloured on account of an absorption band or bands being produced in the visible portion of the spectrum, and physically there is only a difference of degree as to whether the absorption is of radiant energy of short wave-length in the ultra-violet, of medium wave-length in the visible spectrum, or of long wave-length in the infra-red. That a substance exerts selective absorption is probably due to its molecules having oscillation frequencies which correspond to certain wave-lengths of radiant energy, the energy corresponding to such wave-lengths being absorbed by the molecules.

The parent hydrocarbons (benzene, naphthalene, &c.) from which the artificial dyestuffs are derived, are colourless in the ordinarily accepted sense, but, if examined with regard to radiant energy of short wave-length (high-oscillation frequency) are found to exhibit distinct absorption bands in the ultra-violet spectrum (Hartley and Huntington, Phil. Trans. 1879, 170, i. 257; Hartley and Dobbie, Chem. Soc. Trans. 1898, 73, 695; Baly and Collie, *ibid.* 1905, 87, 1332; Hartley, Proc. Roy. Soc. 1908, 80A, 162). The hydrocarbons giving such selective absorption are, in general, members

of the aromatic series, or at any rate possess double linkages in conjugated positions. By substitution, it is possible to so retard the oscillation frequency that an absorption band (or bands) is formed entirely or partially in the visible spectrum. Thus, colourless benzene with its absorption bands entirely in the ultra-violet, may be converted into pale yellow nitrobenzene or into red azobenzene by introduction of a nitro group, or by linking up two phenyls by the azo grouping ·N : N·.

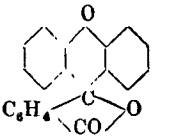
Witt's theory started with facts of this character. Benzene is a colourless substance, but gives coloured derivatives when one (or more) of its hydrogen atoms is replaced by a group known as a *chromophor*. In general, the substance, though coloured, is not a dyestuff; in Witt's terminology it is known as a *chromogen*, since, by the introduction of salt-forming auxochromic groups, a dyestuff may be obtained.

As an illustration, consider the compounds derived from benzene by the introduction of the nitro and hydroxyl groups. Colourless benzene gives pale yellow nitrobenzene, the nitro group conditions the colour of the compound, and is hence known as the chromophor. Since phenol is colourless, the hydroxyl group is not looked on as a chromophor, but it has auxochromic properties. If introduced into the nitrobenzene molecule, a nitrophenol is produced which has distinct dyeing properties, although these are wanting in the chromogen nitrobenzene. (Whilst the mononitrophenols are of no technical importance as colouring matters, trinitrophenol or picric acid can be used as a dyestuff.)

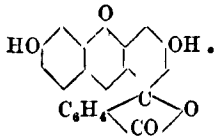
The chief auxochromes are hydroxyl, the amino and the mono and di-alkylamino groups. Although the carboxyl and sulphonic groups are salt forming, they have, as a rule, no auxochromic influence. The alkyloxy groups have a certain auxochromic effect, thus nitroquinol dimethyl ether and other similar compounds possess a yellow colour (Kauffmann, Ber. 1906, 39, 2722, 4237, 4243; Die Auxochrome, Ahren's Sammlung, 1907, xii.).

The auxochromic effect of alkyloxy groups is generally feeble, and an ether is usually lighter in shade than the coloured parent phenolic substance.

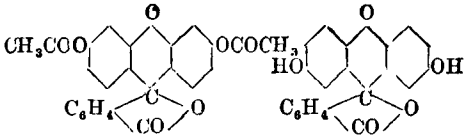
Acylation produces a much greater lightening effect than alkylation. Although amino-groups have a pronounced auxochromic effect which is shared by the mono- and di-alkylated derivatives, acylation of an amino group, as well as its conversion into a quaternary ammonium salt group, inhibits its auxochromic action. The inhibition of the auxochromic properties of hydroxyl groups by acylation may be illustrated by a reference to fluoresceïn. Fluoran, the chromogen of fluoresceïn, is a colourless compound, the introduction of two hydroxyl groups in the positions shown gives the brown compound fluoresceïn, whilst acetylation of fluoresceïn furnishes a colourless diacetyl derivative.



Fluoran (colourless).



Fluoresceïn (brown).



Diacetyl-fluoresceïn (colourless).

Quinol-phthaleïn (colourless).

The examples just mentioned show that the chromogen may itself be devoid of colour, whilst comparison of fluoresceïn with quinol-phthaleïn shows that of two isomeric compounds, one may be coloured and the other colourless, the position of the auxochromic groups in the molecule having a decisive influence in most cases.

Chromophoric properties have been assigned to:

(*a*) The nitro (·NO_2) and nitroso (·NO) groups.

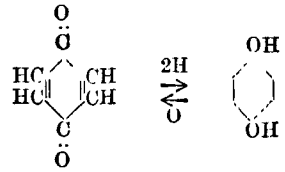
(*b*) The carbonyl (: C : O) and allied groups, *e.g.* : C : S and : C : N·.

(*c*) The azo group (·N : N·) and the nearly related hydrazone configuration, : C : N·NR·.

(*d*) The heterocyclic rings contained in polynuclear dyestuffs.[1]

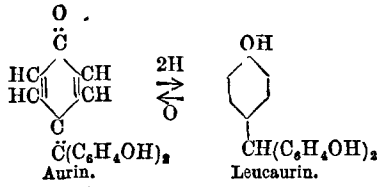
Whilst the chromophor theory has had its uses, difficulties are encountered which necessitate the modification of the original idea that colour is developed in a hydrocarbon structure by the mere introduction of a chromophoric group, the case of the hydroxyl derivatives of fluoran quoted above affording a good example. The difficulty is further increased when one takes into account the fact that coloured hydrocarbons are known. Bisdiphenylene-ethylene (Harpe and van Dorp, Ber. 1875, 8, 1049; Graebe, *ibid.* 1892, 25, 3146) has a red colour which cannot be ascribed to linkage of the benzene nuclei, since diphenyl is colourless. There is difficulty in ascribing chromophoric properties to the grouping : C : C : since stilbene and tetraphenyl-ethylene (Behr, Ber. 1870, 3, 752, and others) are colourless compounds.

A different view as to the relationship between constitution and colour is due to H. E. Armstrong (Chem. Soc. Proc. 1888, 4, 27; 1892, 8, 101, 103, 143, 189, 194; *cf.* Hartley, *ibid.* 1892, 8, 188; and R. Nietzki, Organische Farbstoffe). There are practically no exceptions to the rule that dyestuffs easily take up two atoms of hydrogen, forming the so-called leuco- compounds, which are reoxidised more or less readily to the original coloured substances. The relationship of colouring matter to leuco-compound bears a close resemblance to the relationship of quinone, a coloured compound, to the colourless quinol.



Quinone. Quinol.

[1] Certain non-metals such as iodine may occasionally act as chromophors (H. Ley, Die Beziehungen zwischen Farbe und Konstitution bei organischen Verbindungen, p. 20, S. Hirzel, Leipzig, 1911).



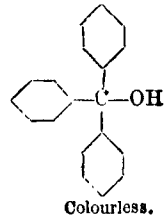
Aurin. Leucaurin.

In fact, the parallelism is so close that a temptation arose not merely to recognise all quinones and quinonoid substances as coloured, but to class all organic coloured substances as necessarily quinonoïd in structure. In certain cases, *e.g.* azobenzene, this led to strange distortion of the usually accepted formulæ, whilst such compounds as hydroxyazobenzene were written with a possibly greater show of reason and probability as quinone-hydrazones. Substitution experiments indicate, however, that hydroxy- and amino-azobenzene and other allied compounds, are not of quinone-hydrazone type, although the salts they form with mineral acids have a quinonoïd structure (*see* Farmer and Hantzsch, Ber. 1899, 32, 3089; Armstrong, Chem. Soc. Proc. 1899, 15, 243; Hewitt, Chem. Soc. Trans. 1900, 77, 99; Hewitt and Aston, *ibid.* 712, 810; Auwers, Ber. 1900, 33, 1302).

Whilst the quinonoïd and chromophor theories have their limitations, no doubt can exist as to the utility of both these ideas in leading to the preparation of new dyestuffs as well as many interesting compounds, amongst which may be mentioned the coloured tetraphenylquinodimethane (1 : 4 bisdiphenylmethylene-$\Delta^{2,5}$-*cyclo*hexadiene)

$$(C_6H_5)_2C : C_6H_4 : C(C_6H_5)_2$$

of Thiele and Balhorn (Ber. 1904, 37, 1463; *cf.* Staudinger, Ber. 1908, 41, 1355). The production of coloured carbonium salts by the action of acids on carbinols, which von Baeyer at one time attributed to the presence of halogen in an ionisable condition (Ber. 1905, 38, 569), is now more frequently ascribed to the assumption of quinonoïd structure.



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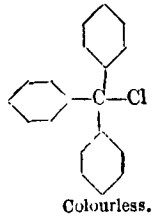
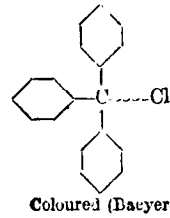
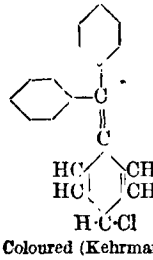


Colourless.



Coloured (Baeyer).



Coloured (Kehrmann).

(*See* Norris and Saunders, Amer. Chem. J. 1901, 25, 54; F. Kehrmann and F. Wentzel, Ber. 1901, 34, 3815; Gomberg and Cone, Ber. 1907, 40, 1847; 1909, 42, 406; Annalen, 1909, 370, 145; K. A. Hofmann, Ber. 1909, 42, 4856; 1910, 43, 183; Flürscheim, Chem. Soc. Trans. 1910, 97, 91.)

In recent years, considerable attention has been paid to the question of what molecular structures would be likely to correspond to more or less definite periods of molecular vibration, thus causing selective absorption; if this absorption is within certain limits of wave-length, visible colour will be produced. In 1900 Hewitt (Zeitsch. physikal. Chem. 34, 1) put forward the view that symmetrical compounds, capable of equal tautomeric displacements in either of two directions, should be those to exhibit the phenomenon of fluorescence, for the molecule would swing between the two extreme positions like a pendulum, the energy absorbed of one wave-length being degraded and given out with slower frequency. This idea was supported by the examination of a number of cases.

In 1904 Baly and Desch (Chem. Soc. Trans. 85, 1029) stated that in the case of tautomeric compounds 'the absorption bands are due to the oscillation between the two isomerides,' and that as a tautomeric compound altered its configuration, so would energy of fairly definite wave-length be selectively absorbed. This idea was based on the observation that whilst metallic derivatives of ethyl acetoacetate show marked selective absorption, the alkyl derivatives, ethyl β-ethoxycrotonate

$$CH_3{\cdot}C(OC_2H_5) : CH{\cdot}COOC_2H_5$$

and ethyl ethylacetoacetate

$$CH_3{\cdot}CO{\cdot}CH(C_2H_5){\cdot}COOC_2H_5$$

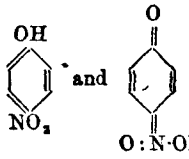
exhibit respectively merely general absorption and transparency at the concentrations and thicknesses examined.

Baly and Desch (Chem. Soc. Trans. 1905, 87, 768) state that 'no organic substance shows an absorption band unless a possibility of tautomerism exists in the molecule. Secondly, this tautomerism need not be due to a labile atom, but may be of the same order as that occurring in those aromatic substances containing the true benzenoid structure. Thirdly, in all cases of the simpler tautomeric molecules, the vibration frequencies of the absorption bands are very nearly the same. Fourthly, an increase in the mass of the molecule causes a decrease in the oscillation frequency of the absorption band.'

At a later date, the idea of tautomeric change had to be somewhat extended since camphorquinone and ethyl pyruvate, compounds in which no tautomerism, in the ordinary sense, can be detected, also show selective absorption. The idea was suggested that in the case of such compounds, rearrangement of linkages occurred which, in the case of ethyl pyruvate, may be represented by the formulæ

$$CH_3{\cdot}\overset{\cdot\cdot}{C}{\cdot}\overset{\cdot\cdot}{C}{\cdot}OC_2H_5 \text{ and } CH_3{\cdot}\dot{C} : C{\cdot}OC_2H_5$$
$$\quad\quad\quad

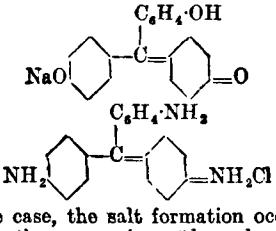
its sodium salt may have a quinonoïd structure; this relationship is exhibited by the formulæ



Study of the absorption spectra of the nitrophenols and their alkaline derivatives led Baly, Edwards, and Stewart (Chem. Soc. Trans. 1906, 89, 514) to agree with this view, but recently, Baly, Tuck, and Marsden have abandoned the hypothesis of quinonoïd transformation on salt formation or ionisation taking place (Chem. Soc. Trans. 1910, 97, 571, 1494). Evidently the structure of these substances must eventually be settled by chemical methods, whilst the isolation of highly coloured labile *aci*-ethers of the nitrophenols by Hantzsch and Gorke (Ber. 1906, 39, 1073), may be adduced as evidence in favour of the quinonoïd structure of the metallic salts.

Hypotheses, involving oscillation of linkages, have been put forward by other authors to explain the colour of certain classes of compounds. Morgan observed colour in the case of certain diazonium salts (Chem. Soc. Trans. 1908, 93, 614; 1909, 95, 1319), which he supposes is conditioned by a rhythmical change of linkage in the molecule which can be represented by the following scheme:—

Von Baeyer (Annalen, 1907, 354, 164) has suggested that the intense colour of the triphenylmethane dyestuffs is conditioned by an oscillation of the quinonoïd linking between two benzene nuclei, the parent quinonoïd substance, fuchsonimonium chloride $C(C_6H_5)_2(:C_6H_4:NH_2Cl)$ not being a dyestuff, although it possesses an orange shade. A further development of these ideas is due to A. G. Green (J. Soc. Chem. Ind. 1909, 28, 638), who points out that the similar crimson-red colour given by aqueous solutions of the sodium salt of aurin and the hydrochloride of rosaniline, are hardly explicable, using the ordinary formulæ for these compounds.



In one case, the salt formation occurs with regard to the non-quinonoïd nucleus; in the other case it is the quinonoïd nucleus that has salt-forming properties. If, however, the sodium and chlorine ion in the two cases be supposed to be oscillating constantly between the two groups, the distinction disappears, for both groups may be considered as engaged in the salt formation.

Meanwhile, it must be remembered that the exhibition of colour is not confined to aromatic compounds; fulvene and its alkyl derivatives are coloured, as are also the fulgides described by Stobbe. In the latter case, it may be mentioned that aromatic derivatives have a deeper shade than fulgides in which only alkyl groups have been introduced.

In every case of coloured compounds, the molecules contain not merely double linkages, but these linkages are in a conjugate position. Generally speaking, the longer the chain of conjugate linkages, the slower the oscillation frequency of the molecule: this was pointed out by Hewitt and Mitchell, in the case of the *p*-nitroarylazophenols (Chem. Soc. Trans. 1907, 91, 1251).

An excellent example of the necessity of conjugate linkages is afforded by ω-azotoluene, described by Thiele (Annalen, 1910, 376, 265). This is a colourless substance. The comparison between this compound and azobenzene and the intermediate compound containing the phenyl and benzyl radicals on either side of the azo-group, is instructive, for the deepest colour is shown by the substance possessing the lightest molecule.

$C_6H_5{\cdot}N:N{\cdot}C_6H_5$	M.W.182	Red crystals
$C_6H_5{\cdot}CH_2{\cdot}N:N{\cdot}C_6H_5$	M.W.196	Yellow oil
$C_6H_5{\cdot}CH_2{\cdot}N:N{\cdot}CH_2{\cdot}C_6H_5$	M.W.210	Colourless crystals

In this case one is considering three compounds, each of which contains the chromophor .N:N· and possesses the same number of double linkages. Here decreasing molecular weight is associated with increase in length of chain of conjugated double linkages, and increasing depth of colour is the result.

An attempt to explain the dependence of oscillation frequency on length of conjugate chain, from a mechanical point of view, has been made by Hewitt (1909, VII. Internat. Cong. of Appl. Chem.). The mass of carbon atoms in such a chain is proportional to the number of double linkages, but should a displacement of linkages occur, the restoring force will not be proportional to the number of double linkages, for whilst the doubly bound carbon atoms move further from one another, those connected by single linkages approach. Hence the ratio of restoring force to mass displaced will decrease with increasing length of chain and the oscillation frequency be diminished in consequence.

Selective absorption must be studied in conjunction with other optical properties, and reference should be made to Lowry's Studies of Dynamic Isomerism, especially to four papers in conjunction with Desch (Chem. Soc. Trans. 1909, 95, 807, 1340; 1910, 97, 899, 905). These deal with an extensive investigation of camphor derivatives, and afford useful evidence of the connection existing between conjugation of double linkages and selective absorption of radiant energy.

The question whether chemical combination is effected by electronic displacement does not come within the scope of this article; that such a conception may form the basis of a theory of selective absorption has been discussed by J. Stark (Phys. Zeitsch. 9, 85), H. Kauffmann (*ibid.* 9, 311) and H. Ley (*op cit.* pp. 68 *et seq.*).

J. T. H.

CHROMOTROPES *v.* AZO- COLOURING MATTERS.

CHRYSANILINE *Diamidophenylacridine* $C_{19}H_{15}N_3$, is obtained as a by-product in the manufacture of rosaniline by the arsenic acid method, and was isolated by Nicholson (Dingl. poly. J. 168, 133) by treating the residue with steam, whereby chrysaniline passes into solution and can be precipitated therefrom by addition of nitric acid. It was further examined by Hofmann (Ber. 1869, 378), who prepared its methyl-, ethyl-, and phenyl- derivatives. Its composition and constitution were first established by Fischer and Körner (Ber. 1884, 203; Annalen, 226, 175; compare also Anschütz, Ber. 1884, 433), who refer its formation in the rosaniline melt to a condensation and subsequent oxidation of orthotoluidine and aniline, since they have effected its synthesis by heating with arsenic acid at 180°–200° the orthodiparatriaminotriphenylmethane obtained by Renouf (Ber. 1883, 1304) by the action of dehydrating agents on a mixture of orthonitrobenzaldehyde and aniline (*v.* also Ostrogovich and Silbermann, Chem. Zentr. 1907, i. 1195).

Properties.—Chrysaniline crystallises with 2 mols. of H_2O from 50 p.c. alcohol in golden-yellow needles, and from benzene with 1 mol. of benzene of crystallisation in golden-yellow scales; the latter melt, when placed in a bath heated at 150°–160°, but when slowly heated lose the associated benzene, and melt, like the former, at 267°–270°. It is insoluble in water, and sparingly soluble in alcohol. On oxidation with chromic acid, it yields acridine and when diazotised is converted into phenylacridine (m.p. 164°). Tetrazo- compounds have been prepared, but their couple products with amines, phenols, &c., are not as good dyes as those obtained from chrysaniline and its salts (Trillat and de Raczkowski, Compt. rend. 114, 1024). Formaldehyde reacts with chrysaniline, yielding an orange dyestuff similar to chrysaniline in its tinctorial properties (T. and de R. Compt. rend. 116, 1382). *Chrysophenol* $C_{19}H_{14}N_2O$, a yellow dye, is obtained when it is heated at 160°–180° with concentrated hydrochloric acid, and crystallises from dilute alcohol with 2 mols. of H_2O in ruby-red needles. Chrysaniline forms two series of salts; of these, the sparingly soluble nitrate is the most characteristic: it crystallises in ruby-red needles, and is employed under various names as a valuable golden-yellow dye for silk, wool, and leather (*v.* ACRIDINE DYESTUFFS).

CHRYSAROBIN $C_{15}H_{12}O_3$ [*Chrysophananthranol* (Hesse, J. pr. Chem. 1908, 77, 383)]. This substance is a constituent, to the extent of 84 p.c. (Attfield), of araroba or Goa powder, the pith of a tree belonging to a species of *Cæsalpina* (Holmes, Pharm. J. [3] 5, 801), and was first extracted therefrom by Attfield (*ibid.* [3] 5, 721), who believed it to be chrysophanic acid, into which, indeed, it is readily converted on oxidation (Liebermann and Seidler, Annalen, 212, 36). Chrysarobin is extracted from Goa powder by hot benzene, and when crystallised from glacial acetic acid forms small yellow laminæ. The constituents of commercial chrysarobin are *chrysophanic acid* (5 p.c.); emodin monomethyl ether (2 p.c.); the *anthranol* of *chrysophanic acid*, 'chrysarobin' (46 p.c.), m.p. 202° (corr.); the *anthranol* of *emodin monomethyl ether* (trace); *monomethyl ether* of *dehydroemodinanthranol* $C_{16}H_{12}O_4$ (18 p.c.); ararobinol $C_{23}H_{16}O_5$ (4 p.c); and an inseparable mixture of substances, together with amorphous material (about 25 p.c.) (Tutin and Clewer, Chem. Soc. Trans. 1912, 290; *cf.* Jowett and Potter, *ibid.*, 1902, 1575). The melting-points of specimens of commercial chrysarobin vary from 170° to 204°, according to the percentage of the constituents present (Hesse, Annalen, 309, 32; and Jowett and Potter, *l.c.*). It can be repeatedly crystallised without alteration, but is oxidised to chrysophanic acid when air is passed through its solution in aqueous caustic potash. On acetylation with acetyl chloride or acetic anhydride, a mixture of the di- and tetra-acetates of chrysarobin is obtained (Knoll and Co., D. R. P. 105871; Chem. Zentr. 1900, i. 524). *Eurobin* is a pharmaceutical preparation, consisting chiefly of the diacetyl- derivative (Hesse, Annalen, 309, 32). It is distinguished from chrysophanic acid by dissolving in concentrated sulphuric acid with a yellow, and in concentrated aqueous caustic potash with a dark-green colour, whilst dilute aqueous potash does not dissolve it; chrysophanic acid, on the contrary, yields a red sclution with concentrated sulphuric acid and dilute aqueous potash (Liebermann and Seidler, Ber. 11, 1603). Another method to distinguish chrysarobin from chrysophanic acid is the following: 0·05 gram of the substance is mixed with 0·2–0·3 gram of sodium peroxide in a porcelain capsule, and 5 c.c. of alcohol are added; after 5 minutes 15 c.c. of water are added. Under these conditions, chrysarobin yields a wine-lees colour, not destroyed by dilution with water, changing to yellow on the addition of acetic acid. Chrysophanic acid yields a cherry-red colour, becoming brighter on dilution (Alvarez, Ann. Chim. anal. 1907, 9) (*v.* ARAROBA POWDER).

CHRYSATROPIC ACID *v.* LACTONES.

CHRYSAZIN *v.* ALIZARIN AND ALLIED COLOURING MATTERS.

CHRYSENE $C_{18}H_{12}$ or $\begin{matrix} C_6H_4\cdot CH \\ C_{10}H_6\cdot CH \end{matrix}$ This hydrocarbon occurs in the highest boiling portions of coal tar, and in the tarry products obtained in the dry distillation of wood, fats, and oils (Laurent, Ann. Chim. Phys. [2] 66, 136). Synthetically, it can be prepared by passing through a red-hot tube the vapour of benzylnaphthylmethane (Graebe and Bungener, Ber. 12, 1078), or those of cumarone and naphthalene, which condense with the loss of a molecule of water (Kraemer and Spilker, *ibid.* 23, 84).

Purification.—Chrysene is extracted from the mixture of solid hydrocarbons consisting chiefly of pyrene and chrysene, which boil at a higher temperature than anthracene, and constitute the last portions of the distillate from coal tar, by repeated digestion with carbon disulphide in the cold. This treatment removes all the hydrocarbons in the mixture except chrysene (present to the extent of 18–19 p.c.), and this is further purified by crystallisation from coal oil (b.p. 150°), from which it separates in golden-yellow scales. The yellow colour, due to an impurity, cannot be removed by repeated crystallisation, but is destroyed by boiling with alcohol and a small quantity of nitric acid (Liebermann, Anhalen, 158, 299).

A second method for obtaining chrysene

from crude greenish-yellow anthracene (m.p. 207°–208°) has been described by Schmidt (J. pr. Chem. [2] 9, 250, 270). For this purpose, 40–50 grams of the anthracene are dissolved in 5 litres of strong (95 p.c.) alcohol, and the solution, after filtration, is boiled with 30 grams of nitric acid (sp.gr. 1·4) in a reflux apparatus for some time. On cooling, red needles of a sparingly soluble compound of chrysene and dinitroanthraquinone $C_{18}H_{12},C_{14}H_6(NO_2)_2O_2$ separate, which, when treated with tin and hydrochloric acid, decompose into chrysene and reduction compounds of dinitroanthraquinone. The hydrocarbon is then obtained pure and colourless by crystallisation from benzene.

Properties.—Chrysene crystallises in scales, or in well-defined, colourless rhombic plates, melts at 250° and boils at 448° (Schweitzer, Annalen, 1891, 193). It is a sparingly soluble substance; for example, 100 parts of absolute alcohol dissolve 0·097 part at 16°, and 0·17 part at 18°, and 100 parts of toluene dissolve 0·24 part at 18°, and 5·39 parts at 100° (*v.* Bechi, Ber. 12, 1978), whilst ether, carbon disulphide, benzene, and acetic acid dissolve it only to a slight extent at the ordinary temperature, but more readily on boiling. The solutions, like the pure hydrocarbon, show a deep reddish-violet fluorescence. On adding chrysene to a solution of formaldehyde and sulphuric acid, a reddish-violet colour is produced; this is destroyed by the addition of water (Ditz, Chem. Zeit. 31, 445). The absorption spectrum of chrysene has been studied by Baly and Tuck (Chem. Soc. Trans. 1902, 14). Chrysene combines with dinitroanthraquinone and with picric acid (trinitrophenol) to form characteristic compounds; the *picrate* $C_{18}H_{12},C_6H_2(NO_2)_3OH$, obtained by adding chrysene to picric acid in benzene solution, crystallises in long red needles, and is decomposed by alcohol (Liebermann, Schmidt). When heated with concentrated sulphuric acid, chrysene yields a sulphonic acid, and when treated with nitric acid, under varying conditions, yields mono, di, and tetra nitro derivatives (*ibid.*), whilst chlorine and bromine convert it into substitution-derivatives (Schmidt). Aminochrysene is obtained by the reduction of nitrochrysene with phosphorus and hydriodic acid (Abegg, Ber. 1893, 792), or with tin and hydrochloric acid (Bamberger and Burgdorf, *ibid.* 1893, 1006). On oxidation with chromic acid in acetic acid solution, chrysene is converted into *chrysoquinone* $C_{18}H_{10}O_2$, which crystallises in yellowish-red needles, melts at 235°, yields azines on treatment with ortho-diamines (Liebermann and Witt, *ibid.* 20, 2242), and is characterised by dissolving in concentrated sulphuric acid with a blue colour.

CHRYSEOLIN *v.* AZO- COLOURING MATTERS.

CHRYSIN, 1:3-dioxyflavone $C_{15}H_{10}O_4$, is obtained from poplar buds (Piccard, Ber. 1874, 88; and Darier, *ibid.* 1894, 21). It has been synthesised by treating phloracetophenone with ethyl benzoate in the presence of sodium, when 2 : 4 : 6-trimethoxybenzoylacetophenone is formed; on boiling with hydriodic acid, the methyl- groups are eliminated, condensation takes place with the production of 1 : 3-dioxyflavones (Emilewicz, Kostanecki and Tambor, *ibid.* 1899, 2448; 1904, 3167). It is a yellow crystalline solid, melting at 275°. By heating it on the water-bath with methyl iodide and potassium methoxide, tectochrysin, which also occurs in poplar buds, is formed (Emilewicz, Kostanecki and Tambor, *l.c.*). Chrysin is a member of the quercitin series (Perkin, Chem. Soc. Trans. 1896, 1443), and dyes cloth mordanted with aluminium a pure yellow; with chromium, an orange-yellow; and with iron, a pale chocolate (Perkin, *ibid.* 1897, 818).

CHRYSOBERYL, *Glucinum aluminate* (*v.* ALUMINIUM).

CHRYSOCOLLA. The Greek name for borax. Now applied to copper silicate (*v.* COPPER).

CHRYSOGEN. An orange-coloured substance, containing more than 94 p.c. of carbon, and said to be a hydrocarbon, discovered by Fritzsche (Zeitsch. Chem. 1866, 139) in crude anthracene. It is sparingly soluble in the ordinary organic solvents. In sunlight, its solutions become rapidly bleached, and yield a colourless crystalline compound which, on fusion, becomes orange-yellow.

CHRYSOÏDINES *v.* AZO- COLOURING MATTERS.

CHRYSOÏN *v.* AZO- COLOURING MATTERS.

CHRYSONAPHTHAZINE *v.* AZINES.

CHRYSOPHANIC ACID $C_{15}H_{10}O_4$ (De la Rue and Müller, Chem. Soc. Trans. 1858, 10, 298; Thanu, Annalen, 107, 324). This acid occurs in the roots of various species of *Rheum* and *Rumex* (H. Grothe, Pogg. Ann. 113, 190). It can be obtained from rhubarb root, in which it occurs together with emodin, by extraction with benzene. After removal of the benzene by distillation, the residue is treated with aqueous caustic soda whereby emodin and other impurities are removed while the acid remains undissolved (Liebermann and Fischer, Annalen, 183, 158). According to Hesse (*ibid.* 1895, 284, 191), it is better to use ether and sodium carbonate instead of benzene and caustic soda in this extraction. The acid obtained from rhubarb always contains the methyl ether of dichrysarobin (Jowett and Potter, Chem. Soc. Trans. 1902, 1575). Chrysophanic acid may also be obtained from chrysarobin by oxidation with air in alkaline solution; the acid is then precipitated by the addition of a mineral acid, and crystallised from petroleum spirit (Liebermann and Seidler, Ber. 11, 1603).

Chrysophanic acid crystallises from alcohol in golden-yellow needles, and melts at 186°–188° (Hesse, Annalen, 1899, 32) at 190°–191° (Grandis, Chem. Zentr. 1892, i. 592; Jowett and Potter, *l.c.*). It dissolves in 1125 parts of alcohol (86 p.c.) at 30°, and in 224 parts at the boiling-point, and is soluble in hot benzene, acetic acid, and amyl alcohol. When heated with zinc-dust, it yields a methylanthracene. Reduction with hydriodic acid yields chrysophanohydroanthranole (Hesse, Annalen, 1896, 305), which has been proved to be identical with chrysarobin (Jowett and Potter, *l.c.*). Concentrated sulphuric acid and aqueous alkalis dissolve it, forming red solutions. Chrysophanic acid can be methylated by means of methyl sulphate and alkali hydroxide (Oesterle, Arch. Pharm. 1905, 243, 434) or by sodium and methyl iodide (Tutin and Clewer, Chem. Soc. Trans. 1910, 6 (*v.* also CASCARA SAGRADA).

CHRYSOPHENIN *v.* AZO- COLOURING MATTERS.

CHRYSOTOLUAZINE *v.* AZINES.

CHRYSOTOLUIDINE $C_{21}H_{21}N_3$. A yellow crystalline base of unknown constitution (*cf.* Hofmann, Ber. 2, 380), occurring in the residue obtained in fuchsin manufacture by the arsenic acid method (Girard, De Laire, and Chapoteaud, Compt. rend. 63, 964; 64, 416). The hydrochloride is a yellow dyestuff.

CHRYSYL. Trade name for zinc boropicrate obtained by boiling together solutions of boric and picric acids with zinc oxide; used as an antiseptic.

CHYMASE *v.* FERMENTATION.

CIDER or **CYDER** is a vinous beverage produced by the fermentation of the juice of apples. Perry is a similar article made from pears. The two are very much alike in character, and, the principles of manufacture being generally the same for each, reference will be made to cider only in this article, except when occasion requires the special mention of perry.

The largest cider-producing country of the world is France, followed by England, Germany, the United States and Canada, and it is now also produced in increasing quantities in other countries, notably Ireland and Australia. In England the principal cider-growing districts are the counties of Somerset, Devon, and Hereford, smaller quantities being made in Gloucester, Worcester, Monmouth, Kent, and Norfolk. The mean annual production of the United Kingdom is estimated at 100,000,000 gallons, of a value of about 3,000,000*l.*

The ordinary cider of commerce in England is a beverage of widely varying character. It may contain as little as 2 p.c. or as much as 8 p.c. of alcohol by weight, depending on the apples from which it is made, and the process of its manufacture, particularly the stage at which the fermentation has been stopped. Apart from its characteristics of flavour, body, and colour, cider may be roughly divided into three classes or grades, viz.: sweet, which has been only slightly fermented; dry, well fermented; and medium, between the two. Apple juice of fair average quality has a sp.gr. of about 1050 to 1055, corresponding to 10–12 p.c. of sugar. As the fermentation produces, roughly, 1 p.c. of alcohol from every 2 p.c. of sugar, the following table shows the approximate comparative composition of apple juice, and the three grades mentioned:—

	Sp.gr.	Sugar	Alcohol
Apple juice .	1050–1055	10–12 p.c.	—
Sweet cider .	1030–1035	6–7	2–2½ p.c.
Medium cider	1015–1025	4–5	3–4
Dry cider .	1000–1010	0–2	5–6

The rough cider of the farmhouse, found in the south-western counties, is of a very dry grade, being fully fermented, no attempt being made to check the 'working,' while the ordinary cider (bottled and draught), found in the average hotel in cities, is a beverage which has been but slightly fermented, and is of the sweet to medium grade, the greatest public demand being for cider as a summer beverage, light, sweet, and refreshing. It must not be assumed, however, that all bottled cider is sweet, for it is obtainable from several firms of repute in four well-defined grades—sweet, medium, dry, and extra dry.

The raw material from which cider is made varies in composition and character as much as the cider itself. The majority of English orchards were originally stocked with almost innumerable varieties of apples and pears, most of them of inferior quality, for either table use or for the manufacture of cider or perry; but great improvements have of late years been made in the planting and cultivation of the orchards, with a corresponding improvement in the quality of the beverages produced. Speaking generally, it may be said that good cider cannot be made from any but essentially vintage varieties of apples, most of which are quite unsuited for table use because of their astringency, due to the large proportion of tannin they contain. The majority of table varieties yield a juice deficient in sugar and tannin, with a large excess of acidity, as compared with the vintage sorts, which are cultivated specially for the manufacture of cider. This is particularly applicable to perry pears, which are almost invariably very astringent in taste, although it is curious to note that the percentage of tannin they contain is not exceptionally high. To make good cider, the sp.gr. of the juice should not be under 1050; it should contain at least 0·15 p.c. of tannin, which gives keeping and clearing properties, with an acidity not exceeding 0·5 or 0·6 p.c. of malic acid, while those substances which constitute 'body,' consisting of mucilage, albumen, salts, colouring matter, &c., are also of importance; but, having been very little investigated, it is impossible to state definitely what proportions of each are necessary. A high sp.gr. with a correspondingly high sugar content, is generally considered the most important quality, but some apples are known to yield a juice high in sp.gr. but deficient in colour and body (the two are usually associated), while others of a low sp.gr. but rich in colour and body, may produce cider of better quality than the first-mentioned. Too much reliance, however, must not be placed on the mere chemical composition of the juice as indicative of the value of an apple for cider making, the characteristic flavour of the variety and the rate of fermentation, which varies greatly with different juices, being at least equally important.

Vintage apples are roughly divided into three classes—sharp, sweet, and bitter-sweet. The following table shows typical analyses of the juice of several of the best of each class, together with that of a hitherto unknown and unnamed variety recently found in Somerset ('Butleigh No. 14'), which is of outstanding merit:—

No.	Variety	Sp.gr.	Malic acid	Tannin	Total sugar
1.	Kingston Black	1060	0·54	0·126	12·66
2.	Foxwhelp .	1059	1·04	0·270	13·25
3.	Cowarne Red .	1054	0·65	0·230	12·05
4.	Sweet Alford .	1057	0·14	0·120	12·19
5.	White Jersey .	1060	0·25	0·190	13·33
6.	Cherry Norman	1055	0·21	0·354	12·25
7.	Horner . .	1053	0·15	0·240	11·89
8.	Royal Jersey .	1065	0·16	0·380	15·00
9.	Barland .	1054	0·62	0·119	11·32
10.	Butt . .	1053	0·66	0·270	11·75
11.	Oldfield .	1068	0·80	0·128	14·92
12.	'Butleigh No. 14'	1104	0·24	0·258	22·22

Nos. 1, 2, and 3 are sharp varieties; 4 and 5, sweet; 6, 7, and 8, bitter-sweet; 9, 10, and 11, perry pears; 12, a bitter-sweet of unusually high quality.

The process of cider making is of very ancient origin, but modern scientific cider making may be said to date from the year 1893, when the Bath and West of England Agricultural Society instituted some chemical and bacteriological research into the subject, a work which was carried on by Mr. F. J. Lloyd for some seven years in Somerset, and has subsequently been continued on a more ambitious scale at the National Fruit and Cider Institute, near Bristol, under the direction of Mr. B. T. P. Barker. The results of these investigations form the foundation of modern cider making, and the reports thereon constitute the most trustworthy literature on the subject.

Whereas the quality of the cider depends primarily on that of the juice used, the nature of the product is largely influenced by the methods of manufacture and fermentation, and general management. The making of cider begins in the orchard, for no good beverage can be made from fruit which has been carelessly gathered or stored. It should be shaken from the trees when just ripe, bruising being avoided as far as possible, and stored in heaps (preferably under cover if the weather be wet), until it becomes soft and mellow, but not over-ripe, care being taken to avoid either washing by rain, which results in the loss of sugar and yeast; or heating, which produces a fustiness in the cider, as well as a great tendency to acetic fermentation. When thoroughly mellow, the fruit is selected and blended in the proportions necessary to give the degree of sweetness, acidity, and astringency required for the variety of cider it is intended to make. Sweet cider is best made from a blend of sweet, sharp, and bitter-sweet apples; while dry cider should be made from a blend giving a minimum of acidity, with only a moderate proportion of tannin. Very few varieties of apples are individually capable of producing the finest cider, an appropriate blending of varieties being necessary. This does not apply to pears and perry making, single varieties, unblended, usually giving best results. In the actual processes of grinding the fruit and expressing the juice, steam-power is generally used in modern factory practice, but, apart from economic reasons, this has no advantage over the old-fashioned hand-power machinery of former days. The fruit is ground to a fine pulp, called 'pomace,' which falls upon the press, is held together in thin squares by manilla or hempen cloths, and is usually pressed at once. In some places, however, the pomace is allowed to remain in tubs for 12 or 24 hours before pressing, which is said to improve the quality of the resulting liquor, but there seems to be no scientific reason for this custom, and investigations have failed to show that sufficient advantages are gained to compensate for the work it entails. With efficient presses, about 70 p.c. of the weight of apples is obtained as juice, and 80 p.c. in the case of pears. The most profitable means of utilising the dry-pressed pomace is as cattle food. In France the juice is sometimes extracted by the 'diffusion' process in use in the beet-sugar industry, but this does not meet with general approval. The fresh juice is run into casks or open vats called 'keeves,' to undergo the important process of fermentation, which commences spontaneously in a few days, the time depending on the character of the juice and the temperature. An important question here arises: Shall the cider be allowed to undergo a natural fermentation, or shall a pure culture of yeast be added to dominate it? At the present time this is a debatable point. While in France and Germany it is generally acknowledged that the use of pure cultures improves the quality of the liquor, and they are largely used, in this country it seems doubtful whether the advantages of their use are sufficient to compensate for the extra expense and trouble involved. Pure yeasts, isolated from the best growths of cider and wine, have been cultivated and added in sufficient quantity to dominate the fermentation and prevent the various wild races from exercising much influence. (Owing to the impossibility of avoiding a cooked taste, sterilisation, even at comparatively low temperatures, is not advisable.) The general results tend to show that fermentation by suitable yeasts gives a somewhat superior product to that obtained by natural fermentation; but the full advantages are not apparent until the cider is about a year old, whereas, in general practice, it is usual for it to be consumed before it attains that age. The use of pure cultures in the cider industry in this country is, for that reason, far from general, and it does not seem likely to make much headway in the present state of our knowledge of the subject. Little is known of the various species of yeasts naturally occurring on the skin of the apple, which subsequently develop in the cider, forming the 'lees' at the bottom, and conducting the fermentation, but the largest number consist of forms allied to the *Saccharomyces Ellipsoideus*, *S. Pastorianus*, and *S. apiculatus* types. A fairly slow fermentation is generally desirable, but, on the other hand, it is one of the most important points in the whole process that the primary alcoholic fermentation be vigorous enough, and is not checked too soon, otherwise the cider is laid open to the attacks of numerous undesirable organisms, which will show their effects in various 'diseases' during the following summer. The 'keeving' system of fermentation, in open vats with loose covers, is preferable to that in closed casks, as the 'head,' which is soon thrown up, consisting of yeasts and light portions of tissue, can be skimmed off from time to time. It is not advisable, however, to keep the cider in the keeves more than about a week, lest incipient acetic fermentation set in, and, as soon as no further head is thrown up, it is racked into closed casks to complete the primary fermentation. The subsequent conduct of this important process is governed by the grade of cider it is desired to make, the hydrometer being in regular use for watching the fall of the sp.gr. The rate of fermentation depends partly on the character and composition of the juice, and partly on the temperature; but these conditions are practically beyond control. Blending the apples to ensure the requisite degrees of sweetness and acidity in the juice will comply with one condition of a moderate rate,

but as the proportion of nitrogenous matter is of still greater importance, and is a subject on which, strangely enough, little is known, and no reliable figures obtainable, blending to ensure the proper percentage cannot be scientifically done. Regulating the temperature is also impracticable, for a large quantity of cider would have to be handled in a very short space of time, and this would be too expensive a process. A large plant would have to be fixed up, which could only be in use a few weeks each year, and possibly it would not be required at *all*. Whenever the sp.gr. approaches the point at which it is desired to stop the fermentation, the cider is racked off into clean casks, with or without sulphuring or the use of other preservative. This alone, however, is not usually sufficient to stop fermentation, unless an excessive quantity of preservative is used, or racking into sulphured casks be repeated several times. The best known means, which has the advantage of adding no materials of a questionable nature to the liquor, is to filter it through one of the many useful cotton-pulp filters now on the market. Even the use of a filter is open to some objections, for it removes some of the body (probably of a colloid nature) and flavour from the cider. The clarification also presents great difficulty with many ciders, neither isinglass finings nor boiled apple pulp, which are commonly used for the purpose, having any effect, so that the filter, which clarifies the cider, and at the same time stops the fermentation, is preferred in the absence of anything better for this purpose. Depending on various circumstances, the cider is filtered and stored away to mature in casks, at any time from two to four or even six months from the time of making. If filtered perfectly bright, and stored in clean casks, kept well filled, it will 'keep its sweets' for a whole season or longer, with the loss of only a few degrees of sp.gr., even though it may contain as much as 6 or 7 p.c. of fermentable sugar. During this period of storage, it *mellows* and develops its fragrant aroma and delicate flavour, and also loses a certain proportion of its acidity and astringency. The strongest and best cider will keep in cask for some years, but that of average quality is at its best within the first year. It keeps best and improves most in bottle, but only cider of good and sound quality should be bottled; it should have an original gravity of at least 1055, should undergo a vigorous primary fermentation, and be perfectly brilliant when bottled. The best age for bottling is from four to six months, and if not more than a year old at the time, it will develop sparkling condition like champagne after a few weeks' storage. The *carbonating* process of bottling is becoming more general, and there seems to be no objection whatever to its use, some of the best brands on the market having been treated in this way.

Matured cider is liable to several disorders or 'diseases,' the principal being acetification, 'sickness,' ropiness, and blackening. It is particularly apt to acetify on very slight provocation, and for this reason, exposure to air at all stages of manufacture is to be avoided. 'Sickness' is a recommencement of alcoholic fermentation, which is set up during the summer following its manufacture, and may occur in cask or bottle. The cider becomes very turbid, and the production of alcohol is accompanied by the development of a most disagreeable smell and flavour, due, it is thought, to formation of acetaldehyde, together with an increase in acidity, partly lactic and partly acetic, which renders the liquor quite undrinkable. It is a source of great loss, for it usually attacks the richest and most fruity ciders, and is due to the action of several special organisms, contributing causes being a deficiency of malic acid in the juice, and a weak primary fermentation. Ropiness is not so frequently met with, and little is known of its causes in cider. Some ciders turn very quickly dark on exposure to air, some almost black in less than half an hour. This may be due either to an excess of iron acquired from the soil or from the utensils used in the making, or to enzymic action; the use of a little preservative often prevents its development.

A standard of chemical composition for what is sold as cider has been formulated in some countries, but not in Great Britain. Owing to the extreme variations in the character and composition of genuine cider, it is almost, if not quite, impossible to fix a definite chemical composition and say that it represents what should be considered a standard cider. For this reason, the standard fixed in foreign countries is necessarily very low, but while it probably admits of a certain amount of adulteration, it no doubt acts as a check. It can hardly be contended that nothing should be sold as cider which is not the pure juice of apples. Brewers, wine makers, and distillers are not restricted by law to the use of malt and hops, grape juice and malt respectively, in the making of their respective products, so that a law to limit cider makers to the use of apples only would operate unfairly against them as compared with the other trades mentioned. It has been stated that many varieties of cider apples grown in this country are not capable of making first-class cider, and the better sorts are in too small a minority to meet the demand. In poor vintage seasons, also, the general quality is low, sugar being deficient and acidity excessive. It is also undoubtedly true that cider made from the poorer varieties of apples, and in poor vintage years, is capable of great improvement by the addition of a certain proportion of cane-sugar syrup, as is done in the process of 'gallisising' wines, to obtain the correct proportion of acidity to sugar. It is difficult to say what maximum proportion of this syrup should be allowed, but there is very seldom any occasion for the use of more than 10–15 p.c. to make the cider suitable for the English market. The fact that there are so-called 'ciders' on the market, which are innocent of a drop of apple juice, shows the necessity for some sort of standard. Generally speaking, it may be concluded that no cider can be considered genuine which does not contain at least 2 p.c. of alcohol by weight, or which does not show an original gravity of 1045 or upwards. Another vexed question is that of the use of preservatives, some people contending that it is impossible to do without them, and others that they are not necessary if the cider be well and carefully made. There is much to be said on both sides. Some makers

sulphur their casks, thus adding a certain quantity of sulphurous acid to the cider; but it is generally considered, though very strangely, that this does not constitute the addition of any 'chemicals.' Others use sulphites or salicylic acid, and justify their use by the argument that all cider, no matter how carefully made, is peculiarly susceptible to various 'diseases' (such as 'sickness' and acetification, previously mentioned), and has often to be kept under conditions which render them unpreventable by any other known means, for example, on draught in a warm bar, perhaps for some weeks. There is certainly a great deal of reason in this, and it would probably be a hardship to absolutely prohibit the use of any preservative; but, on the other hand, they are sometimes used in needlessly excessive quantities, which, in the interests of the public health, should be avoided. The consumption of cider is greatly on the increase, due partly to its being recommended by medical men, and if it is to hold its own as a popular, and above all as a healthful, drink, it must be kept free from any ingredients of doubtful physiological effects.

Appended are analyses of a few typical ciders of well-known makes:—

Description	Sp.gr.	Alcohol by weight	Total acid	Total solids	Ash
Sweet sparkling .	1025	4·65	0·24	5·98	0·245
Standard dry .	1006	3·90	0·31	3 25	0·314
Standard sparkling	1015	3·90	0·53	6·00	0·360
Champagne perry.	1013	4·75	0·35	4·80	0·390

W. D. McC.

CINCHOMERONIC ACID *v.* BONE OIL.

CINCHONAMINE *v.* VEGETO-ALKALOIDS.

CINCHONIBINE *v.* VEGETO-ALKALOIDS.

CINCHONIDINE *v.* VEGETO-ALKALOIDS.

CINCHONINE *v.* VEGETO-ALKALOIDS.

CINEOL *v.* CAMPHORS, SANTONICA.

CINNABAR. Native mercury sulphide (HgS), and the only ore of this metal. Its crystals are rhombohedral, with perfect cleavages parallel to the faces of the hexagonal prism; they are of interest crystallographically in presenting the same type of trapezohedral symmetry as quartz, and, like this, they rotate the plane of plane-polarised light. They are bright-red in colour, often transparent, and have a brilliant adamantine to sub-metallic lustre; the scarlet streak is characteristic. Sp.gr. 8·1; hardness, 2–2½. The massive ore, which may be compact or earthy in texture, is of the same colour; but sometimes it is liver-brown or black, owing to the admixture of clay or organic matter, as in the varieties called respectively *hepatic cinnabar* and *coral-ore* (German, *Korallenerz*). Cinnabar is very sporadic in its distribution, and no mineral containing mercury has yet been found in the British Isles. It is mined at Almaden in Spain; Idria in Carniola; New Almaden, in California; and in the provinces of Kwei-chou and Hunan, in central China. L. J. S.

CINNABAR, AUSTRIAN, *v.* CHROMIUM.

CINNAMALDEHYDE. *Cinnamic aldehyde* $C_6H_5{\cdot}CH{:}CH{\cdot}CHO$, is contained, together with a hydrocarbon, in oil of cinnamon and oil of cassia. It may be extracted from oil of cinnamon by shaking the oil with a concentrated solution of sodium bisulphite, filtering off the crystalline bisulphite compound, washing the latter with alcohol and distilling it with dilute sulphuric acid, when the cinnamaldehyde passes over with the steam. The cinnamaldehyde is extracted from the aqueous distillate with ether, and, after expelling the ether, is purified by distillation under a pressure of from 40 to 50 mm. (Peine, Ber. 1884, 2109). It may be extracted form cassia oil by adding to it the barium salt of sulphanilic acid, filtering off the crystalline compound thus formed and steam distilling, whereby the compound is resolved into its components and cinnamaldehyde distils over (Ch. Fab. von Heyden Akt.-Gesel. D. R. P. 124229; Chem. Zentr. 1901, ii. 903). It is obtained by allowing a mixture of 10 parts of benzaldehyde, 15 of ordinary aldehyde, 900 of water, and 10 of a 10 p.c. solution of caustic soda to stand at a temperature of about 30° for from 8 to 10 days, shaking from time to time:

$$C_6H_5{\cdot}CHO+CH_3{\cdot}CHO=C_6H_5{\cdot}CH{:}CH{\cdot}CHO+H_2O.$$

The solution is extracted with ether and the ethereal extract treated as in the foregoing method (Krszysica, Ber. 1884, 2117). It is best prepared by the condensation of benzaldehyde and ordinary aldehyde at a low temperature by means of a concentrated alkali solution. The alcoholic solution of the aldehydes, cooled to −10°, is agitated with a 25–30 p.c. solution of caustic soda, previously cooled to the same temperature. Under these conditions the formation of resins is avoided (Boehringer and Söhne, Eng. Pat. 10003; J. Soc. Chem. Ind. 1897, 463). Also formed when a mixture of calcium cinnamate and calcium formate is distilled (Piria, Annalen, 100, 105).

It is a colourless oil with a pleasant aromatic smell of cinnamon. It decomposes when distilled under ordinary pressures, especially with access of air, but may be distilled without decomposition in a current of steam or under reduced pressure. It boils at 120°–130° under a pressure of 20 mm. (Peine, Ber. 1884, 2110); at 209·5° under 250 mm. (Perkin, Chem. Soc. Trans. 1896, 1247) and solidifies at −7·5° (Pictet, Compt. rend. 119, 955); sp.gr. 1·0497 20°/4° (Brühl, Annalen, 235, 18).

By oxidation it yields first cinnamic acid and afterwards benzaldehyde and benzoic acid. Direct reduction does not lead to cinnamyl alcohol as the aldehyde polymerises. Reduction with the zinc-copper couple gives rise to hydrocinnamoïn $C_2H_2(OH)_2(CH:CHPh)_2$ (Thiele, Ber. 1899, 1296). It gives the usual reactions of the aldehydes. The diacetyl derivative of the aldehyde, obtained by the action of acetic anhydride, can, however, be easily reduced by iron in acetic acid solution, and by subsequent saponification the alcohol is obtained (Barbier and Leser, Bull. Soc. chim. 1905, 858).

Estimation.—To estimate cinnamic aldehyde in oil of cinnamon or oil of cassia, 10 c.c. of the oil are heated on the water-bath, and a solution of sodium bisulphite added in small quantities, time being allowed for the solid to liquefy between each addition. The precipitate is filtered off and weighed (Schimmel, Chem. Zentr. 1892, i. 92).

Hanuš (J. Soc. Chem. Ind. 1903, 1154) estimates cinnamaldehyde by means of its semioxamazone.

CINNAMEÏN *v. Balsam of Peru*, art. BALSAMS

CINNAMIC ACID $C_6H_5{\cdot}CH{:}CH{\cdot}COOH$. (*Acide cinnamique*, Fr.; *Zimmtsaure*, Ger.) *β-Phenylacrylic acid.* The separation of a solid acid from oil of cinnamon on keeping was first observed towards the end of last century, but the acid was confounded with benzoic acid, until Bizio, in 1826, showed that it was a distinct acid. It was first investigated by Dumas and Peligot (Annalen, 14, 56).

Occurrence.—In liquid storax, partly free, partly as cinnamyl cinnamate (styracin); in tolu and Peru balsams together with benzoic acid and benzyl cinnamate; in some sorts of gum benzoïn; in Barbados aloes; and in the leaves and stalks of *Globularia alypum* and *G. vulgaris*, in the leaves of *Enkianthus japonicus*, and as esters in many varieties of guttapercha.

Formation and Preparation.—It is formed by heating benzaldehyde with acetyl chloride at 120°–130° (Bertagnini, Annalen, 100, 126):

$$C_6H_5{\cdot}CHO+CH_3{\cdot}COCl=C_6H_5{\cdot}CH:CH{\cdot}CO_2H+HCl.$$

Perkin showed that it might be more readily obtained by heating a mixture of benzaldehyde, acetic anhydride, and anhydrous sodium acetate

$$C_6H_5{\cdot}CHO+(CH_3{\cdot}CO)_2O=C_6H_5{\cdot}CH{:}CH{\cdot}CO_2H+C_2H_4O_2$$

(Chem. News, 32, 258; Chem. Soc. Trans. 1877, 388). Edeleano and Budishteano (Bull. Soc. chim. 3, [3] 191) state that by heating 1 part of benzaldehyde, 1 part of acetyl chloride, and 3 parts of sodium acetate for 24 hours at 100°, and subsequently extracting with alkali and precipitating the cinnamic acid with hydrochloric acid, the cinnamic acid is obtained in quantitative yield. The cinnamic acid employed in the preparation of artificial indigo was at first manufactured by this method; but the process was afterwards improved by Caro (D. R. P. 17467 and 18232; Frdl. i. 26), who showed that cinnamic acid could be prepared by heating benzal chloride with dry sodium acetate, thus avoiding the use of the expensive acetic anhydride

$$C_6H_5{\cdot}CHCl_2+2CH_3{\cdot}CO_2Na$$
$$=C_6H_5{\cdot}CH{:}CH{\cdot}CO_2H+2NaCl+C_2H_4O_2.$$

1 part benzal chloride, and from 2 to 3 parts of finely powdered, fused sodium acetate (for which potassium acetate or a mixture of the potassium and sodium salts may be substituted) are heated at 180°–200° for from 10 to 20 hours in an autoclave furnished with a mechanical stirrer. The melt is mixed with water, rendered alkaline with caustic soda, and steam-distilled to remove volatile oils, after which the solution in the retort is filtered hot, and the cinnamic acid is precipitated with hydrochloric acid, filtered off after allowing the solution to cool, pressed, and finally purified by recrystallisation from boiling water or alcohol. A method patented by the Farbwerke vorm. Meister, Lucius and Brüning (D. R. P. 18064), in which lead acetate is substituted for sodium acetate, offers no advantages over the foregoing.

Cinnamic acid may be prepared from benzylideneacetone $C_6H_5{\cdot}CH{:}CH{\cdot}CO{\cdot}CH_3$, which is readily obtained by the condensation of benzaldehyde with acetone under the influence of dilute caustic soda (Claisen, Ber. 14, 2471). When this compound is oxidised by warming it with sodium hypobromite, it is converted into cinnamic acid (Farbwerke vorm. Meister, Lucius and Brüning, D. R. P. 21162; Frdl. i. 28).

By employing substituted benzaldehydes, benzal chlorides, or benzylidene-acetones in the foregoing reactions, substituted cinnamic acids may be obtained.

It may also be prepared from benzaldehyde and malonic acid in the presence of ammonia or amines; in the place of benzaldehyde the benzylidene compounds of certain amines, such as hydrobenzamide, may be used (Knœvenagel, Ber. 1898, 2602; Chem. Zentr. 1898, ii. 695; D. R. P. 97735).

Cinnamic acid may be extracted from storax by boiling in a retort 1·5 kilos. of storax with 2 litres of caustic soda of 24°B. until no more oily drops distil over with the steam. In this process the styracin is hydrolysed, forming sodium cinnamate and cinnamyl alcohol, the latter being volatile with the steam. The aqueous liquid in the retort is separated and the residue repeatedly extracted with boiling water, after which the cinnamic acid is precipitated from the united aqueous solutions by hydrochloric acid and purified by recrystallisation (Beilstein and Kuhlberg, Annalen, 163, 123); Claassen (J. Soc. Chem. Ind. 1897, 932) uses sodium carbonate instead of caustic soda. Precipitated cinnamic acid may be readily freed from adhering resin by recrystallising it from hot light petroleum.

Properties and Reactions.—Forms slender needles or large transparent prisms melting at 133°. Boils at 300° (corr.). If rapidly distilled, it scarcely suffers any decomposition, but by slow heating it is broken up into stryolene $C_6H_5{\cdot}CH{:}CH_2$ and carbon dioxide. Sparingly soluble in cold, more readily in boiling water; easily soluble in alcohol. Forms crystalline salts closely resembling those of benzoic acid. Oxidising agents convert it first into benzaldehyde (distinction from benzoic acid) and afterwards into benzoic acid, the final products when potassium permanganate is used being phenylglyceric acid, benzaldehyde, and benzoic and oxalic acids (Fittig and Ruer, Annalen, 268, 27). When taken internally it is oxidised to benzoic acid, and appears in the urine as hippuric acid. By fusion with caustic potash it yields a mixture of benzoate and acetate. It unites with nascent hydrogen to form hydrocinnamic (*β*-phenylpropionic) acid; with bromine to form a dibromide; and with the hydracids to form *β*-halogenhydrocinnamic acids—thus *β*-chlor-hydrocinnamic acid $C_6H_5{\cdot}CHCl{\cdot}CH_2{\cdot}CO_2H$.

Cinnamic acid condenses with hydrocarbons; thus with benzene and sulphuric acid, it forms phenylhydrindone (Liebermann and Hartmann, Ber. 1892, 2124); with phenols, phenol itself yielding hydroxyphenylcoumarin (L. and H. *ibid.* 1892, 957), and with sulphur to form diphenylthiophene.

Esters. *Methyl cinnamate.* White crystalline solid; m.p. 36°; b.p. 263°.

Ethyl cinnamate may be obtained direct from benzaldehyde by means of ethyl acetate and sodium (Farb. vorm. Meister, Lucius and Brüning, D. R. P. 53671; Eng. Pat. 4946; J. Soc. Chem. Ind. 1891, 358; Claisen, Ber. 1890,

976). It is a colourless liquid, boiling at 226° (corr.) under 250 mm. (Perkin, Chem. Soc. Trans. 1896, 1228). By heating 2 parts of ethyl cinnamate with 1 part of sulphur at 150°–160° for 8 hours, a yellow odourless compound $C_9H_6S_2O$ is formed, and is suitable for therapeutical purposes (Farb. vorm. F. Bayer and Co. Eng. Pat. 8425; D. R. P. 87931; J. Soc. Chem. Ind. 1896, 293; Küster, Ber. 1897, 115).

Benzyl cinnamate v. Benzyl benzoate.

Isomeric acids. *Allo*cinnamic acid, m.p. 68°, two *iso*cinnamic acids, m.p. 38° and 57°, and other isomerides have been described, but a discussion as to their constitution cannot be entered into here. Bülmann (Ber. 1909, 182 and 1443) and Liebermann (*ibid.* 1027) consider that the three acids mentioned above constitute a case of trimorphism.

Substituted cinnamic acids. Of the substitution derivatives of cinnamic acid, the only one of industrial importance is orthonitrocinnamic acid, which is prepared in the manufacture of orthonitrophenylpropiolic acid (*v.* INDIGO, ARTIFICIAL). On a large scale cinnamic acid is first converted by heating with alcohol and concentrated sulphuric acid into ethyl cinnamate. The latter substance, which, being a liquid, is more easily manipulated in the nitration process than the solid cinnamic acid, is run in a thin stream into the calculated quantity of cold nitrosulphuric acid. The mixture of ortho- and para-nitrocinnamic esters thus formed is dissolved in warm alcohol. On cooling, the para-compound crystallises out, whilst the ortho-compound remains in solution. The two ethyl salts are hydrolysed by heating with sulphuric acid. The ortho- acid has also been prepared from *o*-nitro-benzylidene acetone by warming it with a 3 p.c. solution of sodium hypochlorite (Höchster Farb. D. R. P. 21162; Frdl. i. 29). In this process the two isomerides are formed in approximately equal quantity.

Orthonitrocinnamic acid

$$C_6H_4(NO_2)CH{:}CH{\cdot}CO_2H$$

is insoluble in water, sparingly soluble in cold, more readily soluble in boiling alcohol, from which it is deposited in crystals melting at 240°.

The *para- compound* melts at 285°–286°, and is very sparingly soluble even in boiling alcohol. It cannot be used in the preparation of artificial indigo, and the attempt made to utilise it in the rosaniline manufacture has not proved industrially successful.

CINNAMON. The inner bark of shoots of the *Cinnamomum zeylanicum* (Nees), nat. ord. *Lauraceæ*, or true laurels. According to Percival, it is imported principally from Ceylon; but in part also from Madras, Tellicherry, and, rarely, from Java. The bark-peelers select such branches as are 3 years old, and not more than 2 or 3 inches in diameter nor less than half an inch. The bark in drying rolls up into quills, many layers being enclosed in one quill. It is used as a condiment, and yields a highly perfumed essential oil (*q.v.*), employed in the preparation of chocolate and for purposes of perfumery. Both the bark itself in its powdered state and the oil derived from it are frequently adulterated by cassia (*v.* CASSIA).

CINNAMON BROWN *v.* AZO- COLOURING MATTERS.

CINNAMON OIL *v.* OILS, ESSENTIAL.

CINNAMON-STONE or **Hessonite.** A gem-variety of garnet of a warm reddish-brown colour (hence the name) and transparent. It is essentially an orthosilicate of calcium and aluminium $Ca_3Al_2Si_3O_{12}$, containing, however, isomorphous replacements of iron, manganese, and magnesium. Brilliant crystals are found in veins in serpentine at Ala in Piedmont, but material of the best gem-quality is found as pebbles in the gem-gravels of Ceylon.

L. J. S.

CITRAL *v.* TERPENES.

CITRAMALIC ACID *v.* MALIC ACID.

CITRIC ACID $C_6H_8O_7$. *Occurrence.*—This acid commonly occurs in the juice of many fruits, and in the sap of many plants.

Synthesis.—The acid has been prepared artificially by Grimaux and Adam (Compt. rend. 90, 1252). A saturated solution of dichloracetonic acid was neutralised with sodium carbonate, and heated with two molecules of potassium cyanide. The resulting solution of dicyanoacetates was saturated with hydrochloric acid gas, and heated on a water-bath for 15 hours, the citric acid was then separated as calcium citrate by neutralisation with milk of lime. Another synthesis has been effected by Lawrence (Chem. Soc. Proc. 1897, 65), who obtained ethyl citrate by heating together ethyl bromacetate and ethyl oxalylacetate in the presence of zinc.

Properties.—The crystallised acid of commerce has the formula $C_6H_8O_7,H_2O$. The crystals are large prisms belonging to the trimetric system. Their sp.gr., according to Buignet, is 1·553. They deliquesce in damp air, and in perfectly dry air slowly lose the whole of their water. Different crystals (probably differently prepared) may lose water at very different rates (Warington, Chem. Soc. Trans. 28, 928; Grosjean, *ibid.*, 43, 331). According to Marchand (J. pr. Chem. 1841, 23, 60), crystals obtained from a saturated boiling solution have the formula $2(C_6H_8O_7),H_2O$. According to a later investigation by Sarandinaki (Ber. 5, 1100), the crystals from a solution long boiled are anhydrous. Citric acid is optically inactive. The ordinary crystallised acid dissolves in about half its weight of boiling water. Aqueous solutions of various strengths have, according to Gerlach (Zeitsch. anal. Chem. 1869, 295), the following sp.gr. at 15°:—

Acid p.c.	Sp.gr.	Acid p.c.	Sp.gr.
1	1·0037	16	1·0632
2	1·0074	17	1·0675
3	1·0111	18	1·0718
4	1·0149	19	1·0762
5	1·0186	20	1·0805
6	1·0227	21	1·0848
7	1·0268	22	1·0889
8	1·0309	23	1·0930
9	1·0350	24	1·0972
10	1·0392	25	1·0114
11	1·0431	26	1·1060
12	1·0470	27	1·1106
13	1·0509	28	1·1152
14	1·0549	29	1·1198
15	1·0588	30	1·1244

Acid p.c.	Sp.gr.	Acid p.c.	Sp.gr.
31	1·1288	49	1·2153
32	1·1333	50	1·2204
33	1·1378	51	1·2257
34	1·1422	52	1·2307
35	1·1467	53	1·2359
36	1·1515	54	1·2410
37	1·1564	55	1·2462
38	1·1612	56	1·2514
39	1·1661	57	1·2572
40	1·1709	58	1·2627
41	1·1756	59	1·2683
42	1·1814	60	1·2738
43	1·1851	61	1·2794
44	1·1899	62	1·2849
45	1·1947	63	1·2904
46	1·1998	64	1·2960
47	1·2050	65	1·3015
48	1·2103	66	1·3071

A 25 p.c. solution boils at 101·8°, a 50 p.c. solution at 105·8° (Gerlach, J. 1859, 48).

At 15° the solubility of the crystallised acid in alcohol is as follows:—

100 of 80 p.c. alcohol dissolve 87
" 90 " " " 52·85
" 100 " " " 75·90

100 parts of anhydrous ether dissolve 9·1 of the crystallised acid.

According to Buchner (Ber. 1892, 1159), the ordinary hydrated acid melts between 135° and 152°, and the anhydrous acid at 153°. Saltzer (Arch. Pharm. 231, 514) finds that the finely powdered hydrated acid, if slowly heated, becomes anhydrous at 55°, and melts at 160° in this condition.

Decompositions.—When heated to 175°, acetone and carbonic oxide are evolved, the residue is aconitic acid $C_6H_6O_6$; the same acid is formed in small quantity when a solution of citric acid is long boiled (Dessaignes). When heat is continued beyond 175°, an oily distillate appears, which yields crystals of itaconic acid $C_5H_6O_4$. By further heating, itaconic acid is transformed into an uncrystallisable oil, citraconic anhydride $C_5H_4O_3$. Heated with sulphuric acid, carbonic oxide and acetone are given off, and an acid is formed not precipitated by baryta.

Solutions of citric acid are rapidly destroyed by fungi. According to F. Watts (J. Soc. Chem. Ind. 1886, 215), the action of *Saccharomyces mycoderma* on lime juice is to convert the citric acid into carbonic acid and water. According to I. Macagno (Gazz. chim. ital. 11, 443), an alcoholic fermentation in lemon juice does not affect the citric acid, but under the influence of bacteria the citric acid disappears, and acetic and propionic acids are formed.

Salts.—Citric acid is tribasic, and forms in consequence three classes of salts. The salts with the alkali metals are readily soluble in water; the neutral salts of the alkaline earths are only sparingly soluble.

Calcium citrate $Ca_3(C_6H_5O_7)_2,4H_2O$ does not lose water at 100°. When precipitated in a crystalline state its solubility in water is 1 in 1180 at 14°, and 1 in 1730 at 90°–100°. When thrown down in an amorphous condition, the solubility is greater, 1 in 707 at 18°, and 1 in 1123 at 100° (Chem. Soc. Trans. 28, 939).

When a solution of citric acid contains a ferrous, ferric, or aluminium salt, in not too great proportion, it may be made strongly alkaline with potash or soda without producing a precipitate. Such a solution may also be boiled with chalk without precipitating iron or aluminium, although a large part of the citric acid falls as calcium citrate. (With tartaric acid in the place of citric, iron is to a small extent precipitated by chalk in the cold, and entirely on boiling.) If, however, the ferric salt bears a large proportion to the citric acid, the whole is precipitated by chalk, even in the cold (Chem. Soc. Trans. 28, 990).

Derivatives.—Methylenecitric acid is obtained by heating citric acid with four times its weight of polymeric formaldehyde at 140°–160°, and allowing the melt to crystallise. It is used as a disinfectant for the urinary passages (Ch. Fab. auf. Act. vorm. E. Schering, U.S. Pat. 699422; J. Soc. Chem. Ind. 1902, 791).

Monophenetidenecitric acid is obtained by heating 42 parts of citric acid with 27·5 parts of *p*-aminophenetol for some hours at 100°. The product is dissolved in caustic soda, and the acid precipitated with hydrochloric acid. Diphenetidenecitric acid is obtained similarly. They are medicinal substances, acting energetically as precipitants without producing secondary symptoms (Farb. von Heyden-Nachfolger, Eng. Pat. 1254; J. Soc. Chem. Ind. 1895, 385).

Detection.—Citric acid is best recognised when in a pure state by its yielding on heating an oily sublimate, which afterwards crystallises (itaconic acid). A solution of citric acid, neutralised with ammonia, gives no precipitate in the cold with calcium chloride, except after long standing; but on boiling, calcium citrate is precipitated. Calcium citrate, precipitated in the cold, is freely soluble in solution of ammonium chloride, and is precipitated therefrom on boiling. Alkali citrates do not reduce silver salts on boiling, as tartrates do, or only to a trifling extent.

Kämmerer (Zeitsch. anal. Chem. 8, 298) recommends the detection of citric acid by the formation of a crystalline barium salt. To the free acid, or to the alkali salt, excess of barium acetate is added, and the whole heated on a water-bath for several hours; the barium citrate

$$Ba_6(C_6H_5O_7)_4,7H_2O$$

will then be found in microscopic monoclinic prisms.

Dèniges (Compt. rend. 130, 32) adds to the solution $\frac{1}{20}$ of its volume of a reagent obtained by dissolving 5 grams of mercuric oxide in 20 c.c. of conc. sulphuric acid, and 100 c.c. of water. The solution is heated to boiling, and, if citric acid is present, a white precipitate is obtained on the addition of a few drops of a 2 p.c. solution of potassium permanganate.

Another method is to add potassium permanganate to the solution until it is pink. If a precipitate is formed, or a brown colour produced, ammonium oxalate is added until it is destroyed. On adding bromine water a white precipitate is obtained, which, on the addition of alkali, gives the characteristic smell of bromoform (Stahre, J. Soc. Chem. Ind. 1896, 53; Wöhlk, Zeitsch. anal. Chem. 1902, 77).

The tests for adulteration will be given at the close of this article.

Estimation.—When the quantity of citric acid in a solution is determined by alkalimetry, phenolphthalein should be used as the indicator; in coloured solutions red-brown turmeric paper (Thomson, J. Soc. Chem. Ind. 1887, 195) has been recommended. If neutral litmus paper is used, the alkali must be standardised with citric acid. The quantitative determination of citric acid by precipitation as calcium citrate will be described under the analysis of lemon juice.

Citric acid in milk and wine. Citric acid is present in milk and in wine, and as it occurs in small quantities in most wines, adulteration with a small quantity of citric acid cannot be detected (Hubert, Ann. Chim. anal. 1908, 139). It may be detected in milk by taking 10 c.c. of milk, 2 c.c. of sodium metaphosphate, 3 c.c. of mercuric sulphate solution, and filtering. Half of the filtrate is mixed with 0·5 c.c. of 10 p.c. solution of manganese sulphate, and boiled. To this 4 drops of a 2 p.c. solution of potassium permanganate is added, and the solution again boiled. This is repeated, and the liquid decolourised by a drop of hydrogen peroxide. A precipitate or an opalescence indicates the presence of citric acid. This method may be used quantitatively (Denigès, Chem. Soc. Abstr. 1902, ii. 365; *v.* also Scheibe, *ibid.* 1891, 1276). It may be detected in wine by the method of Spica (Gazz. chim. ital. 31, [2] 61). A portion of the wine is evaporated to a syrup and extracted with alcohol. This is nearly neutralised with alcoholic potash, and the potassium bitartrate filtered off. The filtrate is then neutralised with more potash, and the precipitate is filtered off, dried, and heated in a small tube with sulphuric acid, until it goes brown. It is then diluted, made alkaline with caustic potash, and sodium nitroprusside added. A red colour indicates the presence of citric acid. Favrel (J. Soc. Chem. Ind. 1908, 637) evaporates 100 c.c. of wine to dryness, dissolves the residue in 7 c.c. of boiling water, and adds 35 c.c. of 90 p.c. alcohol. A solution of calcium acetate (0·4 gram in 5 c.c. of water) is added, and the precipitate filtered. When dry it is transferred to a test-tube, 3 c.c. of sulphuric acid added, and the whole heated to 80°–90° for 2 minutes. The solution is cooled and extracted with ether. White crystals are obtained, giving a violet-red colour with ferric chloride, the colour being discharged by mineral acids. (For other methods and quantitative estimation, *v.* Williams, Analyst, 14, 25; Devarda, J. Soc. Chem. Ind. 1904, 273; Klinger and Bujard, Chem. Soc. Abst. 1893, ii. 54; Schindler, Chem. Zentr. 1902, ii. 1016; and Robin, Ann. Chim. anal. 1904, 453.)

Raw Material.

Citric acid is prepared from the fruit juice of three species of *Citrus*—the lemon, bergamot, and lime; the first of these is the principal source of citric acid. Concentrated lemon juice is chiefly imported from Sicily; a very little comes from Naples or Sorrento. Concentrated bergamot juice is prepared in Calabria, and exported from Messina. Concentrated lime juice is imported in small quantity from Montserrat and Dominica. The lemon juice from Sicily is prepared by pressing the inferior fruit, from which the rind has previously been removed for the manufacture of essence. The so-called 'single' juice is then boiled down till its sp.gr. equals 60° on the citrometer (sp.gr. 1·24); it then forms a dark-brown, rather syrupy liquid.

Lemon juice has its greatest acidity early in the season (November). The juice of the fine fruit, exported as lemons, has a sp.gr. 1·03–1·04; it contains free acid equal to 11–13 oz. of citric acid per gallon. The inferior fruit pressed in Sicily yields a juice containing at the beginning of the season about 9 oz. of free acid per gallon, and at the end of the season a good deal less.

There are other differences between the juice of fine lemons pressed in England, and the Sicilian juice employed for the manufacture of citric acid. The former contains very little combined organic acid, only about 2·5 p.c. of the total organic acid (free *plus* combined) present. In unconcentrated Sicilian juice the combined acid is about 7–9 p.c. of the total. Again, the English pressed juice contains hardly any organic acid save citric, only about 1 p.c. of the total organic acid being unprecipitable as calcium citrate. In Sicilian juice about 8 p.c. of the total organic acid is unprecipitable as calcium salt.

The concentrated lemon juice from Sicily is reckoned of standard quality when its sp.gr. is 1·24, and its acidity is equal to 64 oz. per gallon of *nominal* citric acid. In dealing with trade analyses it must, however, be borne in mind that the 'crystallised citric acid' of a trade certificate is not the crystallised acid of commerce, but an acid containing only half the actual amount of water, an acid, in fact, having the atomic weight 201 instead of 210:

$$C_6H_8O_7,H_2O.$$

No reason can be given for this practice, which should certainly be abolished. In the present article all quantities of citric acid will be expressed in terms of the common crystallised acid.

The concentrated lemon juice from Sicily contains pretty uniformly 7–8 oz. per gallon of combined organic acid, equal to about 10 p.c. of the total organic acid (reckoned as citric) present. Of the total organic acid about 10 p.c. is not precipitable as calcium salt, and is therefore not citric acid; this proportion is, however, by no means constant. Purchases of lemon juice are unfortunately still made on the basis of acidity, and not on the amount of precipitable acid present. Analyses of 895 pipes of concentrated lemon juice by Grosjean have been published (Chem. Soc. Trans. 43, 333). The average proportion of precipitable acid was 99·2 p.c. of the free acid, but the range of variation was considerable, individual parcels of juice giving 81·1, 85·8, and 103·6 p.c.

Concentrated Bergamot juice has a similar sp.gr. to lemon juice, but a lower acidity; it generally contains free acid equal to about 51 oz. of citric acid per gallon. The quantity of combined organic acid is apparently similar to that in lemon juice, namely, 7–8 oz. per gallon; but the proportion of combined to total is higher, 12–13 p.c. The proportion of unprecipitable acid is about 13 p.c. of the total.

Grosjean's analyses of 90 pipes of bergamot juice show a mean of 98·4 of precipitable acid for 100 of acidity, the extremes being 95·4 and 101·4.

The unconcentrated Lime juice of Montserrat has a mean sp.gr. of 1·036; it contains, according to Conroy (Pharm. J. 1883, 606), an average of 7·84 p.c., or 12·54 oz. per gallon of free acid. The extremes observed were 6·70–10·05 p.c., equal to 10·7–16·1 oz. per gallon. The juice yields 0·43 p.c. of ash. It contains only a trace of sugar. Warington found the combined acid in two samples 5 p.c. of the total; 10 p.c. of the total acid was not precipitable.

Concentrated lime juice is a viscid liquid, sp.gr. 1·32, and with an acidity averaging about 94 oz. of citric acid per gallon. The combined acid is about 8–9 oz. per gallon. The unprecipitable acid is about 10–14 p.c. of the total. The precipitable acid bears a lower proportion to the free than is the case with either lemon or bergamot juice, the published analyses showing a mean of 93·8 of precipitable acid for 100 of free.

The nature of the organic acids, other than citric, present in lemon, bergamot, and lime juice has not been determined. A little formic acid and acetic acid have been detected in concentrated juice, but the principal acids other than citric are clearly non-volatile and have soluble calcium salts. The acids most probably present are malic and aconitic.

Besides lemon juice, some crude Calcium citrate, prepared in Sicily by precipitating lemon juice with chalk, is exported into England. It contains about 64 p.c. of citric acid.

Methods of analysing Juice and Citrate.

1. *Acidity.*—The commercial analysis of juice is confined to the determination of acidity. It is most important that the alkali (sodium hydroxide) used should be actually standardised with citric acid, and the same indicator employed in standardising as in subsequent analyses. Powdered crystals of citric acid are taken, water carefully determined in one portion, while another is used for standardising the alkali. In determining water, the powdered acid should be heated for some hours at about 60° before exposing it to 100°; if this is not done, the acid will melt, and lose the rest of its water with great difficulty. Warington recommended delicate litmus paper for determining the neutral point. F. Watts has since employed films of turmeric tincture on a white tile (J. Soc. Chem. Ind. 1886, 214). Thomson recommends red-brown turmeric paper.

2. *Combined organic acids.*—The juice is neutralised with a known quantity of standard alkali, evaporated to dryness in a platinum basin, the residue gently ignited, the black ash treated with a known quantity (excess) of standard sulphuric acid, the whole boiled and filtered. The amount of unneutralised acid is then determined with alkali. We have now the neutralising power of the ash in terms of alkali; by subtracting the alkali added when neutralising the juice, we obtain the amount of alkali corresponding to the bases of the organic salts, which became carbonates on ignition. From the amount of these bases their equivalent in combined citric acid can be calculated.

3. *Precipitable citric acid.*—This is for the manufacturer the only trustworthy method of analysis, but is, in fact, seldom adopted. Warington proceeds as follows: 15–20 c.c. of unconcentrated juice, or about 3 c.c. of concentrated juice, are exactly neutralised with sodium hydroxide, the solution (about 50 c.c.) is brought to boiling in a salt-bath, and a measured quantity of calcium chloride solution, known to be rather more than sufficient for all the organic acids present added. After boiling for half an hour, the precipitate is collected on a small filter, and washed with hot water. The filtrate and washings are then concentrated to 10 c.c. and the solution finally neutralised with a drop of ammonia. The second precipitate is collected on a very small filter, the filtrate being used for getting the precipitate on to the paper, which is finally washed about five times with a little hot water. The precipitates in their papers are then burnt at a low heat in a platinum basin, and the neutralising power of the ash determined with standard hydrochloric acid and alkali. The amount of citric acid which the base is equivalent to can then be calculated, three molecules of base being reckoned as equivalent to one molecule of citric acid.

4. *Analysis of calcium citrate.*—The excess of chalk present is first determined by boiling about 4 grams with dilute standard hydrochloric acid in a covered beaker, and then adding standard alkali till feebly alkaline. Two grams of the citrate are then gently ignited in a covered platinum crucible, and the neutralising power of the ash determined by solution in standard hydrochloric acid and titration with alkali. By deducting from the neutralising power of the ash that due to the chalk previously determined, we find the amount of base which has to be calculated as citrate. This method presupposes that citrates are the only organic salts present. If it is preferred, the citrate may be dissolved in hydrochloric acid, the solution boiled, neutralised with soda, the calcium citrate precipitated by boiling in the salt-bath, and its quantity determined as in the case of juice.

The information here given respecting juice, calcium citrate, and the methods of their analysis, will be found in greater detail in Chem. Soc. Trans. 28, 925; 43, 331; *v.* also Ulpiani and Parrozzani (Chem. Soc. Abstr. 1907, ii. 57).

Process of Manufacture.

The manufacture of citric acid from concentrated lemon juice is extremely simple. A proper quantity of whiting (levigated chalk) is mixed with water, and heated by steam in a wooden vat provided with a revolving agitator; the concentrated juice is then slowly pumped in, care being, of course, taken that the whiting is finally in small excess. The liquor never becomes neutral, however long boiling may be continued, or however great is the excess of whiting present; the adjustment of juice and whiting is therefore effected by ascertaining if the liquor effervesces with more whiting, or the precipitate effervesces with more juice. The amount of unneutralised acid is about 1–2½ p.c. of the original acidity of the juice. Pure citric acid is readily neutralised by whiting, malic and aconitic acid are not; the final acidity is thus possibly due to the presence of these acids. Citric acid, however, is not

neutralised by chalk if phosphates, and especially ferric phosphates, be present; this fact will also explain the result. It is not advisable to neutralise completely by the use of lime, as vegetable impurities are then thrown down which are afterwards difficult to separate.

The precipitated calcium citrate is washed with hot water on a filter. It is next brought by the addition of water to the state of thin cream, and decomposed, with constant agitation, by the addition of a small excess of sulphuric acid (sp.gr. 1·7). The occurrence of an excess of sulphuric acid is known by the liquor affording a precipitate with a strong solution of calcium chloride after some minutes' standing.

The citric acid liquor is then separated from the gypsum, which is washed on a filter. The liquor is evaporated in shallow leaden baths by steam heat. Much gypsum is at first deposited; from this the clear liquor is run off and further concentrated. When strong enough to crystallise, the hot liquor is run into a wooden tub provided with an agitator, and the liquor is kept in constant motion while cooling; by this process, known as 'granulation,' the citric acid is obtained as a crystalline powder. The mother liquor is again concentrated, and 'salt' again obtained by granulation. The process may be repeated a third time. The liquor is then too dark and impure for further crystallisation, and is known as 'old liquor.' The granulated citric acid when drained, and, if necessary, slightly washed, is redissolved, decolourised by heating with animal charcoal (previously freed from phosphates by hydrochloric acid), again concentrated to the crystallising point, and poured into leaden trays about 3 inches deep; the crystals here formed are the citric acid of commerce. Citric acid thus prepared always contains a trace of lead, and often particles of metallic lead, probably due to the plumbers repairing the vessels. To free the acid from lead, the process usually adopted is to pass sulphuretted hydrogen through the solution after the first crystallisation, filter, and then recrystallise the citric acid in lead-free vessels.

The 'old liquor' is diluted with water, and the citric acid it contains precipitated with an excess of whiting, exactly as in the case of the original juice. The liquor is never neutralised by the whiting; this may be either due to aconitic acid formed during the heating of the citric acid liquors, or to the presence of ferric or aluminic phosphate derived from the whiting.

Any considerable excess of sulphuric acid in the liquors, or any overheating, must be avoided, as occasioning decomposition of citric acid. The presence of iron or aluminium in the whiting also occasions loss, as citric acid holding iron or aluminium in solution is not precipitated by calcium carbonate. In consequence of the non-precipitation of iron or aluminium from citric solutions by whiting, the citric liquors of the factory remain nearly pure, however long the work may have been continued, a result very different from what happens in the case of tartaric acid; the purity of citric-acid liquors is however obtained at the expense of some loss of citric acid. In a well-conducted factory the total loss during manufacture will amount to 12–15 p.c. of the citric acid in the juice.

A method has been patented (Fancheux and Boissière, Eng. Pat. 11991; Fr. Pat. 338735; J. Soc. Chem. Ind. 1904, 680) by which the crude calcium citrate is purified by passing hot gases over it, so as to roast it superficially.

Citric acid is also produced by the fermentation of carbohydrates, glycerol, and analogous substances under the influence of certain fungi, named *citromycetes* (Wehmer, Eng. Pat. 5620; D. R. P. 72957; J. Soc. Chem. Ind. 1894, 275). To prepare the organisms, a sugar solution containing 2–5 p.c. of citric acid is allowed to stand for a few days. The growth formed on this solution is introduced into sterilised sugar, where it develops. The pure culture prepared in this way is then introduced into large vessels containing sugar solution, in which are dissolved small quantities of ammonium nitrate, dipotassium phosphate, and magnesium sulphate; the liquid is then allowed to remain at the ordinary temperature for 8–14 days. At the expiration of that time, the liquid contains a certain amount of citric acid, so that it can be directly employed for lemon juice. The acid can be isolated, preferably as calcium citrate by adding calcium carbonate to the liquid. Other moulds, such as *Mucor piriformis*, which grows on putrefying fruit, specially on pears and apples, may be employed (D. R. P. 91891; *v.* also Maze and Perrier, Compt. rend. 139, 311).

Estimation of lead in citric acid. Forty grams of the sample are dissolved in water, pure strong ammonia added in slight excess, the liquid cooled and diluted to 120 c.c. For a preliminary experiment 10 c.c. are taken, diluted to 50 c.c. in a Nessler tube, and one drop of ammonium sulphide added; the colour determines what volume should be taken; it varies from 5 to 50 c.c. Having repeated this with the volume of liquid thus indicated, the tint has to be matched with that from the pure solution. A volume of pure ammonium citrate solution identical with that taken of the acid under examination is mixed with a measured quantity of slightly acid lead nitrate solution, containing 0·1 gram metallic lead per litre. A drop of ammonium sulphide is added, and various solutions are made up until the colour obtained matches that from the acid under examination. If iron or copper is present in any quantity, a drop of solution of potassium cyanide is added before the ammonium sulphide, which prevents them interfering with the reaction. The standard of purity suggested is that lead is not to be present to a greater extent than 5 parts per million (Warington, J. Soc. Chem. Ind. 1893, 97; *v.* also Tatlock and Thomson, Analyst, 1908, 173).

Another method is that of Buchet (J. Soc. Chem. Ind. 1892, 848). To estimate the metallic lead, 200 grams of acid are dissolved in three times its weight of water, and a slight excess of ammonia added. After 24 hours the liquid is decanted, and the residue collected on a filter, carefully washed and dissolved in nitric acid. The lead is then precipitated as sulphate, and estimated as such. To determine the combined lead, the ammoniacal solution is first acidified with hydrochloric acid, the lead precipitated as sulphide, converted into sulphate, and weighed as such.

Adulteration.—Citric acid is at times adulterated with tartaric acid. To detect adulteration,

Cailletet (Chem. Soc. Trans. 36, 674) adds 1 gram of the powdered acid to 10 c.c. of a cold saturated solution of potassium dichromate. If the solution remains unchanged in colour for 10 minutes, tartaric acid is absent. If tartaric is present, the solution becomes brown. Pusch (J. Soc. Chem. Ind. 1885, 552) places 1 gram of the acid in a test-tube with 10 grams of pure oil of vitriol. The test-tube is placed in a water-bath, and kept at 100° for 1 hour. If citric acid only is present, the colour is lemon-yellow. If tartaric acid is present, the colour becomes brown. Both these tests are very delicate, and readily show 1 or ½ p.c. of adulteration. Piñerua (Compt. rend. 124, 291) puts 0·05 gram of the substance in a porcelain basin, and adds 10–15 drops of a reagent made by dissolving 0·02 gram of β-naphthol in 1 c.c. of concentrated sulphuric acid. If citric acid alone is present, a blue colour is formed, unchanged on heating, which on dilution gives a nearly colourless or a slightly yellow liquid. If tartaric acid is present, the colour on heating changes to green, and on dilution to a reddish-yellow. Denigès adds a small quantity of the acid to a solution of resorcinol in dilute sulphuric acid, and heats to 115°–140°. If tartaric acid is present, a violet-red colour is formed. If sugar is present, or other bodies blackened by sulphuric acid, the acid is precipitated as its lead salt, and then tested (J. Pharm. Chim. 1895, i. 586). Crismer (Chem. Soc. Abstr. 1892, 546) adds 1 gram of the acid to 1 c.c. of ammonium molybdate solution (10 p.c.) and 2 to 3 drops of hydrogen peroxide solution (¼ to ½ p.c.), and heats at 100° for 3 minutes. If citric acid alone in present, the yellow colour given by the molybdate is unaltered; whilst if tartaric acid is present, a beautiful blue colour results. This test detects 1 mgm. of tartaric acid in 1 gram of citric acid. Spindler has modified Denigès' mercuric sulphate method (*q.v.*), and uses potassium dichromate instead of permanganate. If citric acid alone is present, a yellow precipitate is obtained; the presence of tartaric acid is indicated by a change of colour to green, due to reduction. Tartaric acid may also be detected by adding a little solution of potassium acetate to a strong solution of the citric acid, and stirring.

The quantity of tartaric acid in an adulterated sample may be determined by adding 10 p.c. of potassium chloride to a strong solution of the acid, and precipitating the tartaric acid with citrate or acetate of potassium, with the precautions described under estimation of tartaric acid.

CITRIC ACID FERMENTATION *v.* FERMENTATION.

CITRON, OIL OF, *v.* OILS, ESSENTIAL.

CITRONELLA OIL *v.* OILS, ESSENTIAL.

CITRONINES *v.* AZO- COLOURING MATTERS.

CIVET. An odoriferous substance resembling musk or ambergris, obtained from the pouches situated between the anus and genital organs of *Viverra civetta* of N. Africa, *V. Zibetha* of Asia, and *V. Malaccensis* of Java. Is of the consistence of honey, and of a yellowish or brown colour. Contains stearin, olein, mucus, resin, volatile oil, and yellow colouring matter (J. Pharm. 1824, 537). (For analyses of civet, *see* Charabol and Hébert, Bull. Soc. chim. 1910, 7, 687.) Civet melts at about 36°, and contains from 50 to 70 p.c. of fatty acids, and should have a saponification value of about 180°, and should have not more than 1 p.c. of ash.

CLAUSTHALITE *v.* SELENIUM.

CLAY. (*Argile*, Fr.; *Thon*, Ger.) The term 'clay' is ordinarily used to denote certain earths, the chief characteristic of which is that of plasticity when wet, and which have the property of baking to a hard, stone-like mass when heated to full redness. Clay is a heterogeneous mixture of certain hydrated aluminium silicates, with particles of quartz, felspar, mica, &c., resulting from the decomposition of various silicious minerals, the chief source being the felspars of granite rocks. These hydrated aluminium silicates form the essential basis of all clays, and are known as *clay substance* or *clay base*. They are all decomposed by hot concentrated sulphuric acid (*infra*), whilst the other ingredients mentioned above are affected only slightly or not at all. The method of so-called 'rational analysis' is based on this action, and it has been found that when so treated, the great majority of clays give a clay substance approximately of the composition represented by the formula $Al_2O_3{\cdot}2SiO_2{,}2H_2O$. This corresponds with the composition of the rare crystalline mineral *kaolinite*, and, consequently, it has often been assumed that all clays contain kaolinite as their clay base. Within the last few years, however, it has been shown that the clay substance, in some cases, does not correspond in composition with the above formula, and it is now generally accepted that other hydrated aluminium silicates may be present in clays, forming part, and in some cases the whole, of the clay base. Various investigators have attempted to define these substances, and to show that they correspond in composition with certain silicates, such as allophane ($Al_2O_3{\cdot}SiO_2{,}5H_2O$), pyrophyllite ($Al_2O_3{\cdot}4SiO_2{,}H_2O$), halloysite ($Al_2O_3{\cdot}2SiO_2{,}2H_2O+Aq$), pholerite ($2Al_2O_3{\cdot}3SiO_2{,}4H_2O$), &c.

It has been suggested by J. W. Mellor (Trans. Eng. Ceramic Soc. pt. 1, 8) that the term *kaolinite* should be restricted to the comparatively rare crystalline mineral, and that the amorphous clay substance of similar composition ($Al_2O_3{\cdot}2SiO_2{,}2H_2O$) should be called 'clayite.'

The same investigator points out that this latter substance occurs in clays in non-crystalline or amorphous granules, which, however, sometimes show faint polarisation phenomena. Practically all clays contain more or less free silica, undecomposed or partially decomposed felspar, and mica, and they vary in composition through a wide range, differences in composition being brought about partly as a result of different origins, and partly by differences of deposition, &c. The commoner varieties of clay generally contain a considerable percentage of oxide or carbonate of iron, and small percentages of calcium, magnesium, and titanium salts.

Clays may be divided broadly into two classes: residual clays and sedimentary clays. Residual clays are the insoluble residue left from the breaking down and decomposition of rock masses containing certain aluminium silicates (chiefly felspathic minerals), and they

are found overlying or adjacent to the rock mass from which they were formed. These residual clays usually present a gradual change in mineral character from the finer or purer portion nearer the surface to the mixture of clay and undecomposed rock which lies in contact with the rock mass. The decomposition of the mineral silicates may be brought about by the carbonic acid in the surface waters; but many of them are acted on by water alone, and although this action proceeds very slowly, it may account for the gradual decomposition of the felspathic rocks and the formation of clay. The alkalis of the felspars combine with the free silica formed in the decomposition, and with the carbon dioxide contained in the percolating water, forming soluble salts which are more or less completely washed away. In some cases the decomposition of the mineral silicates may have been brought about by the action of gases, and it has been shown by J. H. Collins (Min. Mag. 1887, 7) that when felspar is exposed to the action of hydrofluoric acid, hydrated aluminium silicate is formed, mixed with soluble potassium fluoride, whilst silica is deposited on the sides of the tube in which the reaction takes place. Residual clays, as a rule, contain a smaller percentage of oxide of iron and organic matter than sedimentary clays, and are consequently lighter in colour both before and after baking.

Sedimentary clays are formed by the transportation and redeposition in water of residual clays, and clays so formed may be again transported and redeposited in the same way, so that they may have no direct relationship to the rock formation on which they lie. Sedimentary clays belong to all geological ages, from the present to the Cambrian, and are of varying degrees of hardness, from the soft drift which may be dug with a spade to the hard clay shales of the older formations, which require to be blasted. These clays are always roughly stratified in structure, and show considerable variations in general character and composition throughout their mass, owing to the varying conditions under which they were deposited. The harder varieties of clay are readily converted into the plastic form by grinding with water, or by *weathering*, and they are now largely used for the making of bricks, &c., where formerly only the softer surface clays were used. When breathed upon or moistened, clays usually emit a peculiar odour known as argillaceous. This characteristic is more marked in the sedimentary than in the residual clays, and may possibly be connected with the contained organic matter.

Plasticity is an essential property of all clays in the moist condition, but this quality varies greatly in different clays. The presence of organic matter, finer grinding of the particles of the clay, 'ageing' in the moist condition and 'weathering,' all tend to increase the plasticity, but no entirely satisfactory explanation of the cause of plasticity has yet been put forward. Clay loses practically the whole of its hygroscopic water when dried at 100°, and it contracts and loses its plasticity at the same time, becoming hard and brittle. On being soaked or ground in water, however, it becomes soft and plastic again. The chemically combined water is not driven off until the clay is heated to redness, the temperature of the dehydration, in the case of ordinary clay, being probably between 480° and 600°. Clay that has been heated to this temperature will not again become plastic on being ground with water, so that it is evident that the plasticity of a clay is dependent upon some physical or chemical condition, which is destroyed on heating to about 500°. When clays are heated to a higher temperature (generally about 900°), they contract more or less and become hard, compact, and stone-like, and at higher temperatures still they become vitreous and ultimately fuse. The purest varieties of china clay (which approximate to the composition of kaolinite) fuse at a temperature of about 1830°, and other clays fuse at lower temperatures, according to the nature and percentage of the various impurities contained. The chemical impurities which chiefly affect the fusibility of a clay are the salts of magnesium, calcium, iron, sodium, and potassium. Richter first pointed out that chemically equivalent amounts of the oxides of these substances exert equal influences on the fusibility of a clay. The presence of free silica (quartz sand) tends to raise the fusion point of clays containing a considerable percentage of these bases, but it has an opposite effect on the purer china clays. In the manufacture of pottery ware of all kinds, the firing temperature depends upon the chemical composition of the clay (which determines the fusibility) and upon the result required. For example, in the manufacture of porcelain, where the resultant ware must be non-absorbent or vitreous, the firing temperature ranges from about 1250° to 1550°, according to the chemical composition of the clay mixture or *body* used, whereas in the manufacture of ordinary white earthenware, where a porous or non-vitreous ware is desirable, the firing temperature ranges from about 1150° to 1250°.

The colour of fired clay, *i.e.* clay that has been heated to a temperature of over 900°, depends upon the impurities present, and upon the character of the firing gases. The purer kinds of residual clays fire to a whitish mass, but all other clays become more or less strongly coloured, the tint being determined generally by the percentage of iron oxide present. Iron may be present in clays in various combinations, such as ferric oxide (Fe_2O_3), hydrated ferric oxide ($2Fe_2O_3,H_2O$), ferrous carbonate ($FeCO_3$), and more rarely magnetic oxide (Fe_3O_4), but in firing in the ordinary way all these salts are converted into ferric oxide. Some clays contain a considerable amount of iron pyrites disseminated through the mass in small grains, and these clays are often troublesome in use, as the sulphide is not so readily converted into oxide in the ordinary firing process. Moreover, the sulphide on weathering with the clay gives rise to soluble sulphates which are detrimental. In the yellow and brown surface clays and red-firing shales, the iron is present in the form of ferrous carbonate, which, together with the organic matter present, produces the natural grey colour of these shales. In ordinary clays, and with an oxidising atmosphere, 1–2 p.c. of iron oxide produces a buff colour, 2–4 p.c. a salmon colour, and above 4 p.c. a red colour, which becomes darker as the percentage of iron increases. The

presence of other impurities, however, modifies the colour produced by iron oxide considerably, and this is especially the case when a large percentage of lime or magnesia is present.

Some clays (commonly called marls) contain from 15 to 30 p.c. of lime, and although they may also contain as much as 6–8 p.c. of iron oxide, they fire to a light-yellow or buff colour. Such clays are largely used for making the well-known yellow facing bricks, which were at first made chiefly from the marls of the Thames basin, the Paris basin, &c., and are now made from artificially prepared mixtures of clay or chalk and limestone. The presence of certain soluble salts (chiefly sulphates of calcium or magnesium) in clays often produce serious discolouration on firing, owing to the deposition of these salts on the surface during the drying and firing of the ware. To prevent this action, it is usual to mix with the clay barium carbonate, to combine with the whole of the sulphuric acid present, and so convert the soluble salts into insoluble ones. When clays are fired in a reducing atmosphere, the red ferric oxide is converted into blue ferrous oxide, and the resultant ware is consequently bluish in colour. Blue bricks are made from certain clays, containing generally from 6 to 10 p.c. of iron oxide by firing in this way.

The presence of clay in soils exerts an important action on the growth of plants. Ammonia is retained by clay in such a manner that it cannot be removed except by an excessive amount of washing; in fact, clay will remove ammonia and many organic substances from manure, and still retain them in a form readily available for plants.

Kaolinite $Al_2O_3 \cdot 2SiO_2, 2H_2O$. A comparatively rare crystalline mineral which occurs in Anglesey, in Colorado, and a few other localities in the form of minute hexagonal plates, having a perfect basal cleavage, and belonging to the monoclinic system. Kaolinite was formerly supposed to form the base of all clays, but this view is no longer held, and the term should be restricted to the crystalline mineral described above.

Kao-lin, China clay. The Chinese term 'kao-lin' (literally meaning 'high ridge') was applied to the white earth from which porcelain was made, and it corresponds to the English china clay, so called because it is used for the making of 'china,' or porcelain. These terms are now applied to all the purer residual clays which contain a high percentage of hydrated aluminium silicate ($Al_2O_3 \cdot 2SiO_2, 2H_2O$), and which consequently give on analysis 33–40 p.c. alumina (Al_2O_3), 45–60 p.c. silica (SiO_2), 11–14 p.c. water, with very small percentages of iron oxide, soda, potash, lime, magnesia, &c. Clays of this class are worked in Cornwall and Devon, at St. Yrieix near Limoges, Zettlitz in Bohemia, in the United States, in South Africa, &c. As mined, the clay generally contains a large percentage of quartz-sand and mica, and it is refined by washing. In Cornwall the china clay is usually the result of the weathering of pegmatite, and the felspar of the parent rock is often decomposed to a depth of 60 to 100 feet. In this condition it is known as *china clay rock*, and the workman breaks down the crumbling surface with a pick and then directs a stream of water over this to wash down the material, which is passed into tanks where the suspended matter settles out, the quartz, clay, and mica being deposited according to the sizes of the particles, and so separated from each other. The china clay is allowed to dry to a stiff paste in the tanks, and is then removed to the drying kilns, where it dries until it can be cut into blocks ready for shipment. It is a soft, friable, sectile, white substance, showing irregularly shaped granules under the microscope, and possessing only a moderate plasticity when mixed with water. China clay is used in the manufacture of porcelain and white earthenware, in paper making, and the *filling* of calico, and also in the manufacture of alum, aluminium sulphate, and ultramarine. The fine mica separated from the china clay in the washing is used for weighting coarse papers, paper boards, &c.

Ball clay, Potter's clay. The name given to certain sedimentary clays which fire to whitish or light-buff colour, and which possess high plasticity and tensile strength when in a moist condition. They are worked in Devonshire and Dorset, and in some parts of the United States, &c., and are chiefly used in the manufacture of white earthenware. They are generally finer in grain then china clay, contain more organic matter and other impurities, and are consequently more plastic in a moist state, and fire to a vitreous mass at a lower temperature. They usually also contain a higher percentage of silica than china clays.

Pipe clay. A rather loose term, which is applied to white clays which contain a relatively high percentage of silica, and which have been used without admixture for several hundred years for the making of tobacco pipes and also for common pottery. These clays are of various geological origins, and in some localities the highly silicious clay found in pockets in limestone formations, and resulting from the decomposition of argillaceous limestone and chert rock, is used in this way. Ball clay is also used for the same purposes, and is sometimes consequently spoken of as pipe clay.

Plastic clay. This term has been specially applied to those beds of the Lower Tertiary or Eocene strata, which occur between the London clay and the chalk, and which may be recognised at Woolwich, Reading, Blackheath, Bognor, and in the neighbourhood of Paris, &c. This clay is mottled red or purple, and fires to a red colour. Some of our earliest pottery was manufactured from this clay, and it is still worked in Hampshire, in the Isle of Wight, and elsewhere.

Slate clay occurs in Devon, Cornwall, &c., differing considerably in different districts. It is massive, interspersed with mica, and of a greenish or greyish colour. It is sometimes hard and *slatey*, being readily cleavable into slabs, whilst in another form, the killas of the Cornish mines, it has an earthy fracture, is soft and frangible, and weathers to a more or less plastic clay. It is chiefly used for the manufacture of common bricks and tiles, and, when fairly free from lime, magnesia, and iron, for fire-bricks.

Common clay is the term often applied to

the ordinary surface and drift clays which have been used for centuries for making common pottery and bricks.

Fireclays. As the name implies, these clays are of a very refractory nature, and although, strictly speaking, practically all the pure residual clays come under this head, the term 'fireclay' has been restricted in use to certain coal-measure shales which have a high fusion point, and which are used mainly for the manufacture of firebricks, gas retorts, glass pots, furnace linings, &c.

These fireclays usually underlie the coal seams, and are often worked in conjunction with the coal. Certain districts are particularly noted for the quality of their fireclays, and in England the Stourbridge coal-measure shales have long been considered of the highest quality, and fireclay-mines are extensively worked in the Stourbridge district. Good fireclays are also found and worked in the Lancashire and Yorkshire, Derbyshire, and Glasgow coal-fields. The fireclay shales are mostly greenish-grey in colour, compact, dense, and of varying degrees of hardness. On exposure to the weather they usually crumble down, and in time become converted into plastic clay. The weathering process may be greatly accelerated by grinding the shale, but this is only done when the clay is to be used for the more expensive fireclay goods. Only those coal-measure shales which contain small percentages of oxide of iron, lime, and magnesia, are sufficiently refractory to be used as fireclays, and although no definite fusion-point has been fixed, it seems advisable that no clay having a fusion-point lower than 1500° should be classed as a fireclay. In the manufacture of fireclay goods, the partially weathered or ground fireclay is usually mixed with a certain proportion of 'ganister,' coarse sand, burnt clay, or other refractory material which produces in the fired ware a certain open texture, which enables it better to withstand rapid changes of temperature. Certain silicious fireclays and other coal-measure clays are used in the manufacture of salt-glazed drain pipes, and also for making common culinary ware, buff-coloured tiles, terracotta, glazed bricks, &c.

Chemical analysis of clay. From 1–2 grams of finely powdered clay, dried at 120°, are weighed into a platinum crucible, and mixed with about six times its weight of a fusion mixture consisting of potassium and sodium carbonates in equimolecular proportions. The mixing is best performed by first stirring together the clay with about the same bulk of fusion mixture by means of a dry glass rod, and then adding more and more fusion mixture with repeated stirring, until the whole is thoroughly mixed. The glass rod should then be rubbed in a little fusion mixture, which is added to the mass in the crucible. The covered crucible is gradually heated over a Bunsen burner (a Teclu burner may be advantageously used) until the whole mass is in a state of tranquil fusion. The crucible is allowed to cool, and afterwards the bottom is raised just to dull redness, twice successively, in order to facilitate the removal of the mass from the crucible. After cooling, a few drops of distilled water are added, and the crucible very gently warmed until the mass detaches itself. The contents of the crucible are then washed into a large platinum dish (a porcelain dish may be used without seriously impairing the accuracy of the estimation), covered with water, and then warmed until the fused mass is completely softened. Hydrochloric acid is then added, a few drops at a time, until all effervescence ceases. The contents of the dish are evaporated on a water-bath, with constant stirring at the later stages, to ensure a fine powdery residue from which the last traces of hydrochloric acid are readily driven off. When cold, the contents of the dish are moistened with moderately strong hydrochloric acid, and allowed to stand for one hour; water is then added, and the dish again heated on the water-bath. The clear liquid is poured through a filter, and the residue in the basin, which consists of silicic acid, is washed repeatedly by hot water until it remains white when moistened with hydrochloric acid. The residue is then transferred to the filter, and washed with hot water until the filtrate no longer gives a precipitate with silver nitrate solution. The filter and contents are then placed in a platinum crucible and dried, and afterwards gradually heated, and finally ignited strongly until the paper is completely incinerated, and the weight constant. In order to ensure the complete separation of the silicic acid, it is necessary to evaporate the filtrate down to dryness, and treat exactly as before, and this process may be repeated again if very great accuracy is required. After filtering, the filter paper and residue are dried and added to the original silicic acid residue before ignition. The contents of the crucible are then weighed as silicon dioxide (SiO_2). If the clay contains titanic acid (as many clays do), this will accompany the silica. In order to determine the former, the contents of the crucible are covered with strong hydrofluoric acid, a few drops of sulphuric acid added, and the crucible warmed on the water-bath until all the silicon fluoride and the sulphuric acid have been driven off. The residue is then weighed as titanic oxide (TiO_2), which should be identified by the violet-coloured bead with microcosmic salt.

The filtrate is made up to definite volume, and divided into two parts, one for the determination of the iron, and the other for the determination of the alumina, calcium, and magnesium. The iron is estimated as ferric oxide, and determined either by reduction with zinc and titration with potassium permanganate solution, or by the iodimetric method.

The other portion of the filtrate is heated on the water-bath, and ammonia added drop by drop, with repeated stirrings, until there is a *slight* excess of ammonia present. The liquid is then boiled for a moment and filtered. The precipitate is washed twice with hot water; washed back into a dish, and dissolved in hydrochloric acid; reprecipitated and filtered as before, and finally washed with hot water until the filtrate gives no precipitate with silver nitrate solution. The washing should be repeated immediately the previous washing has disappeared from the filter, and a jet of hot water should be directed into the precipitate so as to break it up as much as possible. The filter paper and contents are then dried, the residue removed into a platinum crucible, the paper separately incinerated, and then placed in the

crucible, and the whole strongly ignited until the weight is constant. The contents are then weighed as alumina (Al_2O_3) and ferric oxide (Fe_2O_3), the amount of ferric oxide separately determined as above being deducted from the total, leaving alumina only (art. ALUMINIUM). The filtrate from the alumina and ferric oxide is concentrated, and ammonium oxalate solution added while hot. The precipitate is filtered off, thoroughly washed with hot water, dried, strongly heated, and weighed as CaO. The filtrate from the above is then concentrated, and the magnesium precipitated by sodium phosphate and ammonia. The precipitate is filtered off, dried, and ignited until the weight is constant. The ignited residue consists of $Mg_2P_2O_7$, and the weight must be multiplied by 0·3624 to give the amount of magnesia (MgO) contained.

Determination of the alkalis. The method introduced by Lawrence Smith (Amer. J. Sci. [2] 50, 269) is the most trustworthy, and is based on the decomposition of silicates by fusion with calcium carbonate. In practice, the dried and finely powdered clay is mixed with its own weight of ammonium chloride, and four times its weight of calcium carbonate. These latter materials must be as free as possible from alkali. The ammonium chloride used is prepared by subliming the commercial salt; and the calcium carbonate is prepared by dissolving the purest calcite obtainable in hydrochloric acid, and precipitating with ammonia and ammonium carbonate. The precipitation is carried out in a large porcelain dish, and, after settling, the clear liquid is poured off, and the precipitate washed by decantation until free from chlorides. A special platinum crucible is used for the fusion, about 8 cm. long, and 2 cm. diameter at the top, tapering to 1½ cm. at the bottom. About 0·5 gram clay is weighed out, and mixed by rubbing in an agate mortar with the same weight of ammonium chloride, and afterwards 3 grams of calcium carbonate are added, and the whole thoroughly mixed. The mixture is then transferred to the crucible, and the mortar is cleaned out with about 1 gram of calcium carbonate, which is added to the mixture in the crucible. The covered crucible is supported in an inclined position, and very gradually heated over a small Bunsen flame for about 15 minutes, until no more ammonia is given off, and then the temperature is raised until the lower three-fourths of the crucible is a dull-red, and this temperature is maintained for 1 hour. The crucible is cooled and the contents removed (by tapping the inverted crucible) into a porcelain or platinum dish. If the sintered mass sticks to the crucible, a little water should be added, and the crucible gently warmed until the mass detaches itself, and the whole can be washed into the dish. About 60 c.c. of distilled water are added, and the covered dish heated on a water-bath for 30 minutes, the water lost by evaporation being replaced, and the larger particles reduced by rubbing with an agate pestle. The clear liquid is decanted through a filter, and the residue washed by decantation four times, and then transferred to the filter and washed until the filtrate gives no precipitate with silver nitrate. The filtrate contains the alkalis as chlorides.

The calcium is precipitated by the addition of ammonia and ammonium carbonate to the filtrate, which is heated and filtered. The residue, which contains some alkali, is dissolved in hydrochloric acid, again precipitated by ammonia and ammonium carbonate, and filtered. The combined filtrates are then evaporated to dryness in a platinum dish, and the ammonium salts removed by careful heating over a moving flame. The residue is dissolved in water, and any traces of calcium left are precipitated by the addition of ammonia and ammonium oxalate. After standing 12 hours, the liquid is filtered off, evaporated to dryness in a weighed platinum dish, and gently heated. The alkali chlorides remaining in the dish are weighed, and the potassium determined by dissolving the chlorides in water and precipitating the potassium as potassium platino-chloride. The sodium is determined by difference.

Rational analysis of clay. To determine the relative amounts of clay substance, quartz, and undecomposed felspar, dry the clay to constant weight, and weigh about 5 grams of the dried and finely powdered clay into a porcelain dish; add 50 c.c. of concentrated sulphuric acid and 100 c.c. of water, and then heat the mixture for 3 hours on a water-bath, and afterwards on a sand-bath, until the acid commences to fume. After cooling add water, and decant the clear liquid into a 2-litre beaker. To the residue in the dish add 10 c.c. of Lunge's solution (100 grams crystallised sodium carbonate, and 10 grams sodium hydroxide, dissolved in 1 litre of water), boil for 5 minutes, dilute with water, and decant into the beaker. Treat the residue in the dish similarly with concentrated hydrochloric acid, and repeat the treatment with Lunge's solution and hydrochloric acid, diluting with water after each treatment, and decanting the clear liquid into the beaker. Then wash the residue on to a filter with dilute hydrochloric acid. Stir up the contents in the beaker, and allow to stand for an hour. Decant off the clear liquid, taking care to retain the residue in the beaker. Wash the residue into the dish, and repeat the treatment with Lunge's solution and acid as above, and pass through the filter. Wash with dilute hydrochloric acid, dry and ignite the filter paper and contents in a weighed platinum crucible. This residue is reckoned as felspar and quartz, and the loss suffered by the clay in this treatment as clay substance.

To determine the quartz and felspar, add about 5 c.c. of water, 4 drops of sulphuric acid, and 15 c.c. of hydrofluoric acid to the residue in the crucible, and heat the whole carefully on a sand-bath until nearly dry. Add more hydrofluoric acid, and again heat as before. After cooling, dissolve the mass in water, wash into a dish, and add ammonium chloride and ammonium hydrate to precipitate the hydroxides of aluminium and iron. Filter, wash with hot water, heat and weigh. This weight is multiplied by 5·451 to obtain its equivalent in potash felspar, and the difference between this and the weight of the original residue is taken as quartz.

Many ceramic chemists calculate the rational constitution of the clay from the ultimate analysis, taking the potash as derived

entirely from undecomposed felspar (reckoned as $K_2O \cdot Al_2O_3 \cdot 6SiO_2$), the alumina and iron as derived from felspar, and the clay substance (reckoned as $Al_2O_3 \cdot 2SiO_2, 2H_2O$) and the silica as derived from the clay substance and quartz.

J. B.

CLAY IRONSTONE *v.* IRON, ORES OF.

CLAY SLATE *v.* SLATE.

CLAYTON CLOTH RED, *v.* AZO- COLOURING MATTERS.

CLAYTON YELLOW *v.* PRIMULINE AND ITS DERIVATIVES.

CLEVEITE. A variety of uraninite, consisting of a uranate of uranyl, and oxides of lead and the rare earths. Usually obtained from Norway and Sweden. Hillebrand (Bull. U.S. Geol. Survey, 78, 43, 83) found the percentage of rare earths to be about 13, and that on heating with sulphuric acid, over 2 p.c. of nitrogen was evolved. Ramsay (Chem. Soc. Trans. 1895, 1107) proved that the gas evolved was not nitrogen, but helium (*q.v.*). Only half the helium is evolved by heat alone, and, moreover, in some cases the disengagement of the gas is accompanied by considerable evolution of heat (Proc. Roy. Soc. 1898, 64, 140).

CLICHY WHITE. A white lead manufactured at Clichy, in France (*v. White lead*, art. LEAD).

CLOTHBROWN, -ORANGE, -RED, -SCARLET, *v.* AZO- COLOURING MATTERS.

CLOVE OIL *v.* OILS, ESSENTIAL.

CLOVER. The name by which several leguminous forage plants are known. The chief species are: white clover (*Trifolium repens*, Linn.); red clover (*T. pratense*, L.); alsike clover (*T. hybridum*, L.); crimson clover (*T. incarnatum*, L.); yellow suckling clover (*T. dubium*, Sibth.); mammoth red, or zigzag clover (*T. medium*, L.); hop clover, or hop trefoil (*T. procumbens*, L.). All the above belong to the true clovers, to the genus Trifolium. Also included as clover are: yellow clover, or trefoil (*Medicago lupulina*, L.); Bokhara clover, or melilot (*Melilotus alba*, Desn.); Japanese clover (*Lespedeza striata*, Hook. et Arn.); and Soola clover, or sulla (*Hedysarum coronarium*, L.). The following table gives the average composition of various clovers at the time of flowering (Kellner):—

	Water	Protein	Fat	Sol. carbohydrates	Fibre	Ash
T. repens	81·5	4·4	0·8	6·9	4·3	2·1
T. pratense	79·0	3·4	0·7	9·4	5·9	1·6
T. hybridum	81·8	2·8	0·7	7·0	6·2	1·5
T. incarnatum	81·5	2·8	0·7	7·0	6·1	1·9
T. procumbens	80·0	3·5	0·8	8·4	5·7	1·6
Melilotus alba	79·7	4·1	0·8	7·4	5·7	2·3

The following are analyses of hay from various clovers:—

	Water	Protein	Fat	Sol. carbohydrates	Fibre	Ash
T. repens	9·7	15·7	2·9	39·3	24·1	8·3
T. pratense	16·5	13·5	2·9	37·1	24·0	6·0
T. hybridum	16·0	13·6	3·1	34·5	25·7	7·1
T. incarnatum	16·7	12·0	2·4	35·5	26·2	7·2
T. procumbens	16·0	15·4	3·4	33·2	24·5	7·5
Melilotus alba	15·7	16·7	2·8	27·9	30·3	8·0
Lespedeza striata	9·1	13·7	4·0	47·5	21·6	4·1

White or Dutch clover is a low, creeping perennial plant, valuable for grazing. Its growth in pastures is encouraged by phosphatic and potash manuring, but discouraged by nitrogenous manures. In America, it is said that its blossoms salivate horses, and that consequently much clover in pastures is an objection where horses graze. White clover furnishes most excellent pasturage for bees, the honey which it yields being colourless and of high quality.

Red clover or broad clover is usually grown as a biennial, but will sometimes stand longer. It is often grown as a hay crop, or for cutting for green forage. It is the variety most susceptible to 'clover sickness,' and on many soils can only be grown safely once in 10 or 12 years.

A variety of red clover, *T. pratense* var. *perenne*, known as 'cow grass,' is not so prone to clover sickness, and lasts longer. It is, however, of slower growth, and usually yields but one crop per year of hay.

Alsike clover has whitish and pinkish flowers, and is a perennial; it is hardly susceptible to clover sickness.

Crimson clover, or 'trifolium,' is also a somewhat slow-growing crop, and is an annual.

Yellow suckling clover is a smaller plant than the other clovers, and is usually only grown in mixtures with rye-grass, &c. It is an annual.

Zigzag clover, known in America as mammoth red clover, ripens later than red clover, and is taller and ranker.

Bokhara clover, or large white clover, is a biennial, with small white flowers. This plant is remarkable for its strong odour, more pronounced when dried, of coumarin; animals do not eat it readily until they become accustomed to it.

Soola clover is a perennial resembling red clover, but is richer in soluble carbohydrates (*v.* Scurti, Chem. Zentr. 1910, i. 1632).

As the table of analyses shows, clovers are remarkable for the large amounts of nitrogenous matter and of ash which they contain. Of the former, however, a considerable proportion is of a non-protein nature, particularly in the immature plants. In the case of red clover, for example, it has been found that about 40 p.c. of the total nitrogenous matter is present as amides in very young plants, and that the proportion diminishes with growth, until, when the plants are in full bloom, it is about 20 p.c., when fully ripe it sinks to about 12 p.c.

The ash of clovers is remarkable for its richness in lime and its poverty in silica (in which grasses and cereal straws are so rich).

The following are Wolff's analyses of various clover ashes:—

	K_2O	Na_2O	MgO	CaO	P_2O_5	SO_3	SiO_2	Cl
Red clover	34·5	1·6	12·2	34·0	9.9	3·0	2 7	3·7
White ,,	19·4	7·8	10·0	33·2	14·1	8·8	4·5	3·2
Alsike ,,	33·8	1·5	15 3	31·9	10·1	4·0	1·2	2·8

The very high ratio of lime to phosphorus pentoxide in the ash is noticeable.

Clover hay has proved very successful as a constituent of the rations of fattening oxen and sheep.

Out of about 200 feeding experiments with nearly 1000 cattle, conducted in Britain between 1833 and 1908, 17 included clover hay in the daily ration. The average daily increase in live weight per head of the whole was 1·803 lbs., while the consumption of total digestible matter per 1 lb. live weight gained averaged 9 lbs. In the 17 cases where clover hay formed a portion of the food, the figures are 2·1 lbs., and 7·47 lbs.

respectively (Ingle, Journ. High. and Agri. Soc. of Scotland, 1909).

With sheep, the results are equally significant. 2390 sheep fed in various ways, between 1844 and 1909, gave an average weekly increase per head of 2·06 lbs., and consumed an average of 7·43 lbs. total digestible matter per 1 lb. increase in live weight; while 384 sheep receiving clover hay as part of their ration, gave an average weekly increase of 2·58 lbs. per head, and consumed only 6·20 lbs. of total digestible matter per 1 lb. increase in live weight (*ibid.* 1910).

H. I.

COAL *v.* FUEL.

COAL GAS *v.* GAS, COAL.

COBALT. Sym. Co. At. wt. 58·97.

Cobalt usually occurs combined with arsenic or sulphur, and almost invariably associated with nickel and other metals. Free cobalt occurs only in meteorites.

The most plentiful and important ore of cobalt is *smaltine* or *tin white cobalt*, consisting of arsenide of cobalt, nickel, and iron. It occurs abundantly at Schneeberg and many other localities where bismuth is found (*v.* BISMUTH), in Bohemia, at Balmoral near Pretoria, near Sudbury in Ontario, very pure at Tunaberg in Sweden, and free from nickel in Colorado. As triarsenide, it forms *skutterudite* $CoAs_3$. Sulpharsenide of cobalt occurs as *cobalt glance, grey cobalt*, or *cobaltine*, abundantly at Vena (Sweden) and in Norway; in smaller quantities in Silesia and Cornwall. As hydrated arsenate it forms *cobalt bloom* or *erythrite* $Co_3As_2O_8$,Aq., found frequently as a peach-coloured incrustation on other arsenical ores, being produced by their decomposition. As sulphide, cobalt occurs in small quantities in *cobalt pyrites* and in *linnalite*.

Black earthy cobalt is a hydrated oxide of cobalt and manganese. It is essentially a variety of *wad* (hydrated manganese oxide), containing sometimes as much as 40 p.c. of cobalt. Surface deposits containing oxides and sulphides of cobalt and of nickel occur at New Caledonia, with veins of chrome ore and nickel and magnesium silicates; it is smelted on the spot and exported as a regulus to England. Cobalt occurs in small quantities in many other minerals; in pyrites and in certain iron ores; as oxide in black oxide of manganese; as arsenide in mispickel, sometimes to the extent of 10 p.c.; in selenide of lead, and in cerite, and in some peats and coals.

At the present time the most important source of cobalt, whence almost the whole of the cobalt of commerce is obtained, is the district surrounding Cobalt city, near the shores of Lake Tamiskaming in North Ontario. Here very rich silver ores are found, containing frequently 2000 oz. silver per ton, and sometimes as much as 60 p.c. These ores also contain a high percentage of cobalt and nickel, chiefly as arsenides, and, after extraction of the silver in Canada, are exported to nickel and cobalt refiners.

Extraction.—The methods adopted by manufacturers for the extraction of cobalt from the ores vary with the nature of the ores. The ores are first concentrated by fusing with a suitable flux, whereby silicious matter and a portion of the iron are removed. In the case of the Ontario ores, the speiss consists chiefly of arsenides of cobalt, nickel, iron, and copper. The speiss is then calcined, the iron is oxidised to ferric oxide, part of the arsenic is removed, a little less being left than is required to combine with the iron. The mass is then dissolved in hydrochloric acid, and lime is added, whereby the iron is precipitated as arsenate and hydroxide. The liquid is then treated with sulphuretted hydrogen to precipitate copper and other heavy metals, excess of the gas evaporated off, and the cobalt precipitated as oxide by the addition of bleaching powder. The nickel in the solution is subsequently precipitated by potash or lime.

In the case of New Caledonian ores, consisting chiefly of sulphides, the treatment of the concentrated ore is somewhat different. The *matt*, consisting chiefly of sulphides, is carefully calcined at a moderate temperature, and converted into sulphates. These are dissolved in water, and the iron precipitated by careful addition of the requisite quantity of sodium carbonate. The copper and heavy metals are separated by sulphuretted hydrogen, and after boiling off the excess, the cobalt is precipitated by sodium hypochlorite (bleaching powder cannot be used, owing to the sulphates in the solution), and the nickel in the remaining liquid precipitated by sodium carbonate.

In Herrenschmidt's process for the treatment of New Caledonian ores, these are treated with a solution of ferrous sulphate, when cobalt, nickel, and manganese pass into solution, and iron remains in the residue. Copper is first separated, and then the cobalt, nickel, and manganese precipitated by sodium sulphide. The manganese is extracted by ferric chloride, the nickel and cobalt sulphides roasted to sulphates, and converted into chlorides by calcium chloride. A part of the solution is treated with lime water, and the suspended precipitate oxidised by chlorine and added to the other portion, whereby the cobalt is precipitated and nickel chloride remains in solution.

Metallic cobalt is not at present used to any extent in the arts, though its utility is becoming more fully recognised. Commercially it is always prepared by heating the oxide with charcoal; it then contains small quantities of carbon. Pure cobalt is prepared by heating cobalt oxalate $Co(CO_2)_2$, when the carbon and oxygen pass off as carbonic anhydride, leaving the pure metal as a powder. A button of the fused metal may be obtained by fusion of the oxalate alone, or of the oxide mixed with charcoal under a layer of powdered glass containing no lead or other reducible metal; the fusion is preferably performed in a lime crucible at the highest temperature of a furnace. Pure cobalt may also be prepared by electro-deposition with platinum electrodes (Winkler, Zeitsch. anorg. Chem. 8, 1). Cobalt is also produced as a grey metallic powder by igniting the oxide at a red heat in a current of hydrogen. If too low a temperature has been used, the metal produced is *pyrophoric*, igniting and becoming reoxidised in contact with the air.

Properties.—Cobalt is a brilliant silver-white metal, similar in properties to iron. It is the most magnetic metal after iron, and retains its magnetism at high temperatures; above 1115° it passes into a non-magnetic variety.

Pure cobalt is harder and more tenacious

than iron, its breaking weight being about 50 kilos. per sq. millimetre. Valenciennes states that cobalt, after fusion and annealing, may be rolled into spiral bands like good iron (Compt. rend. 70, 607). Cobalt melts at 1530° (Copaux), *i.e.* about the temperature at which English hammered iron fuses. Its sp.gr. is 8·8, and hardness, 5·5. Its specific heat (20°–100°) is 0·104; specific resistance, 5·5; and the temperature coefficient of resistance, 0·0055. It is slowly soluble in hydrochloric and sulphuric acids, with evolution of hydrogen, quickly soluble in nitric acid; it is not attacked by hot or cold alkali, but if used as anode in the electrolysis of alkaline electrolytes, passes into a colloidal solution of cobaltous oxide. It exhibits also the *passive* state, similar to that of iron and other metals, but the tendency to do so is slight. Cobalt occludes from 60 to 150 times its own volume of hydrogen, the amount varying with the mechanical condition of the metal. The powdered metal combines, when heated, with chlorine, bromine, and iodine. It decomposes steam at a red heat, and, if finely divided, ignites when heated in oxides of nitrogen, and in a current of ammonia gas at 500° forms a nitride Co_4N_2. When finely divided cobalt is heated to 150°–200° in carbon monoxide at 100 atmos. pressure, orange-red crystals of *cobalt carbonyl* $Co(CO)_4$ are formed, melting at 51°, soluble in alcohol or ether, but insoluble in water, and decomposing above 52°, *yielding* $Co(CO)_3$ which further decomposes (Mond, Chem. Soc. Trans. 1910, 798) (*v.* COBALT CARBONYLS).

Cobalt may be deposited as a fine lustrous coating on metals by the electrolysis of a neutral solution of the double sulphate of cobalt and ammonium, using a current of about 6 amperes per sq. foot of cathode surface, and an anode of cobalt (A. Gaiffe, Compt. rend. 1878). The presence of ammonium chloride appears to hinder, whilst ammonium sulphate assists, the deposition. The deposit of cobalt is harder, more tenacious, and of greater beauty than that of nickel (Troost).

(For the properties of cobalt containing other metals, *v. Alloys of cobalt.*)

Detection.—All ores and compounds of cobalt impart a blue colour to a bead of borax on fusion; if present in too great excess, the bead appears black. Heated on charcoal with reducing flux, all substances containing cobalt produce metallic particles which are attracted by a magnet (distinction from all other bodies except iron and nickel).

Salts of cobalt, when *strongly* heated with alumina before the blowpipe, give a fine blue colour (Thenard's blue). Sulphuretted hydrogen produces no precipitate in an acid solution, but gives a black precipitate of sulphide in alkaline solutions, the precipitated sulphide being insoluble in dilute acids. In a solution containing free acetic acid, potassium nitrite produces a yellow precipitate of potassium cobaltinitrite $K_3Co(NO_2)_6$; the whole of the cobalt being thus precipitated on standing in a warm place for some time. If a mineral acid is present, it should first be neutralised by potassium hydroxide.

Potassium thiocyanate with cobalt salts gives a red colouration, and, on the addition of alcohol and ether, forms a deep *blue* ethereal layer.

Cobalt is also precipitated as a red precipitate by the addition of a solution of nitroso-β-naphthol to its alcoholic or acid solutions. As nickel is not thus precipitated, this forms a useful means of separation of the two metals, the sulphides being dissolved in *aqua regia*, evaporated to dryness, taken up with a little water and hydrochloric acid, and precipitated as above.

Estimation.—Ores containing cobalt are usually very complex; they almost invariably contain nickel and many other metals from which the separation is difficult. The following scheme will serve for the estimation of both cobalt and nickel in any mineral, though in the case of certain ores it may be somewhat simplified.

From 2 to 7 grams of the finely ground ore are roasted in a porcelain crucible in a muffle. The residue is boiled with hydrochloric acid containing a little nitric acid until the metallic oxides are dissolved; the solution is diluted, nearly neutralised with ammonia, and boiled with sodium acetate solution, whereby the iron and aluminium are precipitated as acetates containing the greater part of the arsenic (as arsenate of iron) and a little nickel and cobalt. The solution is filtered, and the precipitate redissolved in hydrochloric acid and reprecipitated as before, the precipitate being this time free from nickel and cobalt. The two filtrates are mixed, just neutralised with ammonia, and treated with sulphuretted hydrogen gas; cobalt, nickel, zinc, copper, bismuth, &c., are thus precipitated as sulphides, leaving the manganese and the alkaline and earthy metals in solution. The precipitate is filtered, washed, dried, and roasted, the oxides so produced dissolved in hydrochloric acid, and treated with sulphuretted hydrogen; the copper, bismuth, lead, &c., are thus precipitated and filtered off.

The solution is boiled till free from sulphuretted hydrogen, and the two metals co-precipitated by the addition of potash to the boiling solution; the precipitate is filtered and washed, nearly dried, and separated as far as possible from the filter. The precipitate is digested in a dish with dilute hydrocyanic acid, then with potash solution, and again with hydrocyanic acid, and warmed until no further solution occurs. A minute quantity of residue is left, consisting of paracyanogen and a small quantity of the oxides of nickel and cobalt; it is added to that still remaining on the filter paper, and the whole washed, dried, heated, and weighed.

The solution containing the two metals is boiled to expel the excess of acid, and consists of cobalticyanide of potash and double cyanide of nickel and potash. Precipitated yellow mercuric oxide is added, and the solution boiled for some time. The nickel is thus precipitated, partly as cyanide and partly as sesquioxide. It is filtered, washed, dried, heated, and weighed as nickel protoxide NiO. The filtrate is nearly neutralised with nitric acid, and a neutral solution of mercurous nitrate added in excess. The cobalt is thus precipitated as mercury cobalticyanide, which is washed, dried, and heated in an open crucible until of constant weight. The product consists of Co_3O_4.

From the proportions of cobalt and nickel thus found, the amount of each in the residue on the filter paper, &c., which has been weighed

may be calculated, and added to the amounts directly determined.

In other methods, the copper, &c., are first precipitated by sulphuretted hydrogen, iron by ammonia, and the nickel and cobalt precipitated as sulphides. The sulphides are redissolved, and in (1) the total nickel and cobalt estimated by electro-deposition; in (2) the cobalt is first precipitated and the nickel alone determined.

The cobalt in the above solution may also be determined by precipitation as potassium cobaltinitrite, dissolving the precipitate in warm dilute sulphuric acid, evaporating nearly to dryness, and electrolysing after addition of ammonium oxalate and excess of ammonium carbonate (Copaux Bull. Soc. chim. iii. 29, 301).

The solution containing the sulphides of nickel and cobalt may also be estimated after freeing from excess of acid by boiling with barium carbonate, and adding excess of bromine water. After 10 minutes the cobalt is completely separated as sesquioxide (Taylor, Proc. Man. Phil. Soc. 46, 1).

Various volumetric methods have been suggested, but none appears to be perfectly satisfactory.

Alloys of cobalt. Cobalt unites with incandescence on fusion with *antimony* or *arsenic*, forming brittle iron-grey alloys.

With *arsenic* the freezing-point curve indicates the existence of compounds, Co_5As_2; Co_2As; and Co_3As_2. Smaltine $CoAs_2$ forms tin-white octahedra; and *skutterudite* $CoAs_3$ occurs as greyish-white octahedra. The arsenides are attacked by oxidising agents, and all containing over 38 p.c. arsenic are non-magnetic.

Antimony and cobalt are completely miscible in the liquid state. Three classes of alloys exist: magnetic alloys with less than 67 p.c. antimony; alloys of from 67 to 80·27 p.c., which on heating form CoSb; and alloys above 80·27 p.c., which by acids yield a compound, $CoSb_2$, as a grey crystalline powder (Ducelliez, Compt. rend. 147, 1048).

Cobalt has a marked effect on the electrical properties of *copper*; 3·5 p.c. gives an alloy with a temperature coefficient of the resistance of only 0·00077. Two series of mixed crystals appear to exist, 0–10 p.c., and 95–100 p.c. copper, and alloys within these limits consist of conglomerates of the two sets of mixed crystals. Some of the alloys are very ductile. As in many of the cobalt alloys at high temperatures, the cobalt is present as a non-magnetic form (β), which changes to the magnetic (α) form on cooling. Alloys containing 99 p.c. of copper are stated to be magnetic (Sahmen, Zeitsch. anorg. Chem. 57, 1).

Tin and cobalt are perfectly miscible as liquids, and, according to Ducelliez (Compt. rend. 148, 502), all alloys are mixtures of CoSn and Co_3Sn_2 with one another, or with either of the components. Below 57·6 p.c. tin, the alloys are magnetic and brittle; above 66·8 p.c. tin, the alloys are less brittle and non-magnetic; all are much harder than either component. A compound Co_2Sn of m.p. 1151° has also been described.

With *gold* a brittle alloy is produced, that containing 1 part gold and 17 parts cobalt is dark-yellow and very brittle; all the alloys are magnetic. With *platinum* a fusible alloy is produced; and a silver-white magnetic amalgam with *mercury* is used in dentistry.

Alloys with *aluminium* containing less than 68·5 p.c. cobalt are non-magnetic, the freezing-point curve indicates a compound CoAl. Cobalt and nickel do not appear to form a compound; the freezing-point curve is almost straight, the composition of the solid being almost identical with that of the liquid in all cases.

Addition of *iron* has no appreciable effect on the melting-point of cobalt, the curve being almost horizontal to 5 p.c. cobalt, the crystals having the same composition as the fused mass. Two series of non-magnetic, which transform into four series of magnetic crystals, appear to exist (Tammann, Zeitsch. anorg. Chem. 45, 205). Steels containing up to 60 p.c. cobalt show perlitic structure, and the mechanical properties are only slightly affected by the cobalt.

Lead, *silver*, or *bismuth* are only partially miscible with cobalt when molten, and no definite alloys appear to be formed.

With *silicon* in the electric furnace, steel-grey metallic-looking silicides are formed, Co_2Si and $CoSi_2$. Both are stable and hard, and attacked by hydrofluoric acid and *aqua regia*. A very hard magnetic *boride* is prepared in a similar manner; and by the action of phosphorus on cobalt chloride at a low red heat a hard brittle *phosphide*, Co_2P_3, not affected by heat or acids, is produced.

It is possible to combine cobalt or nickel with manganese with the production of valuable alloys. For this purpose commercial manganese or ferro-manganese may be used, the presence of iron not being injurious. From 2 to 5 p.c. of the manganese is added in small portions to the molten metal; much gas is evolved after each addition, and the metal is poured into moulds when tranquil (*v.* Huntingdon, J. Soc. Chem. Ind. 1882, 258).

It is stated that when in the molten condition cobalt and nickel take up both carbon and oxygen, but evolve the greater part of the latter substance on cooling, leaving a porous metal containing carbon. A method has been patented whereby this carbon is said to be eliminated. The porous cubes of metal are immersed in a 4 p.c. solution of alkaline manganate or permanganate, dried and melted in a crucible at a high temperature. The carbon is said to be thus oxidised and removed, and the metal takes up a small quantity of oxygen. As soon as the metal flows easily, a little black flux and charcoal, or a small quantity of aluminium, or the calcium zinc produced in Caron's process, is added, and the oxygen thus removed (Dingl. poly. J. 1884, 254–315).

Oxide of cobalt is used for the preparation of the salts of cobalt and of smalt, and by enamellers and porcelain manufacturers for the production of the finest blue glaze and colour on porcelain, glass, and other vitrifiable substances. The presence of $\frac{1}{2500}$ of this substance imparts a bluish tinge to clear glass.

The presence of other oxides has an injurious effect on the colour produced by this substance (*v. Smalt*); it is therefore necessary, for the more delicate work, to ensure its complete freedom from such impurities.

When heated strongly with magnesia, it produces a pink mass; with alumina, a fine blue

(Thenard's blue); and with zinc oxide, a green (Rinmann's green). *Zaffre* consists of a very impure oxide of cobalt, produced by roasting the ore. It is usually mixed with 2 or 3 parts of fine sand or ground quartz, and is used for the same purpose as smalt for the coarser work.

Cobalt blue, Cobalt ultramarine, Thenard's blue, Azure blue. The composition of this pigment varies considerably, according to the method of manufacture. It consists sometimes of the oxides of cobalt and aluminium; at other times it contains phosphate or arsenate of cobalt.

It is best prepared by first precipitating a solution of a cobalt salt, usually the nitrate, free from iron and nickel, with potassium or sodium phosphate, or with sodium arsenate. The gelatinous violet precipitate is thoroughly washed and well mixed with 3–5 volumes of freshly precipitated, well-washed alumina (when cobalt arsenate is employed, a larger proportion of alumina may be added), precipitated from a solution of alum free from iron by the addition of sodium carbonate. The mixture is dried until it becomes brittle, and calcined at a cherry-red heat for 30 minutes in a well-covered clay crucible. When the desired blue colour has been developed, the mass is ground with water and dried. In order to prevent the possibility of entrance of reducing gases, which much injure the value of the product, Regnault recommended the addition of a little mercuric oxide before the ignition. This becomes decomposed and evolves oxygen, which effectually prevents reduction, while the mercury escapes as vapour (Regnault, Cours Elém. de Chimie, 3, 150).

A similar but less fine colour is produced by the simultaneous precipitation of the oxides of cobalt and aluminium by the addition of sodium carbonate to a mixture of cobalt nitrate and alum; the mixed precipitate is washed and treated as above.

According to the process recommended by Binder (Technologiste, 5, 55), the oxide of cobalt is precipitated by the addition of the requisite quantity of ammonia to a solution of pure cobalt chloride. The washed precipitate is mixed with alumina as before, dried, and calcined at a red heat in a clay crucible for two hours.

Thenard's blue is of a fine ultramarine colour; the presence of excess of cobalt imparts a somewhat greenish tinge. It has, however, the disadvantage of appearing violet by gaslight. It is one of the most permanent blue pigments, being unaltered by acids or alkalis, and is largely used as an oil and water colour, but works better as water colour. It is non-poisonous, and has the advantage of miscibility with other pigments without alteration.

Cœruleum, *Cœline, Bleu céleste,* is a corresponding colour containing oxide of tin and usually calcium sulphate. Its general composition is said to be oxide of tin, 49·66; oxide of cobalt, 18·66; calcium sulphate and silica, 31·68; and a pigment of this nature is obtained by precipitating a solution of cobalt nitrate with sodium stannate, and heating the precipitate as above.

It is a fine light-blue pigment of slightly greenish tinge, of greater density than Thenard's blue, and retains its colour in artificial light.

New blue. A blue pigment of shade varying from a pale-greenish blue to a deep-turquoise blue, largely used for enamels, consists of aluminates of cobalt and chromium produced by the action of alum on carbonates and hydroxides of cobalt and chromium.

Cobalt green, *Rinmann's green.* The constitution of this pigment corresponds with that of Thenard's blue, with the substitution of zinc oxide for alumina.

It may be prepared by mixing a solution of pure cobalt sulphate (or nitrate) into a paste with zinc oxide, and heating in a muffle furnace for 3 or 4 hours, until the desired colour is obtained. Pigments of a more uniform nature are produced by the precipitation of a mixture of solutions of zinc and cobalt salts, by means of sodium carbonate, phosphate, or arsenate, drying and heating the precipitate. The phosphate is said to give a purer and brighter green than the carbonate.

R. Wagner (Technologiste, 18, 409) gives the composition of fine green pigments as varying from 71·68 p.c. zinc oxide and 11·62 p.c. cobalt oxide, to 88·04 p.c. zinc oxide and 11·52 p.c. cobalt oxide, the quantity of phosphoric oxide also varying greatly.

Rinmann's green is a fine permanent pigment; its colour varies through many shades, according to the proportion of zinc present, the darker greens containing less of that substance. It is non-poisonous and unacted upon by dilute acids or alkalis, but is attacked by ammonia. It has also the advantage of not affecting or being unaffected by other pigments. Rinmann's green, on account of its high price, and the number of other permanent greens, finds little use as a pigment. Another permanent green pigment used in porcelain painting is said to be prepared by the calcination of a dried mixture of the following proportions of the freshly precipitated substances: 20 cobalt carbonate, 40 alumina, 20 chromium oxide.

Cobalt bronze is a phosphate of cobalt and ammonia, of a violet colour, with a bronze-like metallic lustre.

Cobalt silicates. A cobalt silicate is produced by the addition of sodium silicate (soluble glass) to a cobalt salt. It produces a blue pigment well suited for painting on glass and porcelain.

Smalt. *Bleu d'azur, Bleu de Saxe.* This important substance consists of a silicate of cobalt and potash.

In the preparation of smalt in Saxony, smaltine is principally used. In Norway and Sweden the principal ore is cobaltine. The general process is identical for both ores.

The selected ore is powdered, freed from the lighter earthy impurities by washing, and placed, in charges of about 3 cwt., in a layer of 5 or 6 inches thick on the bed of a reverberatory furnace or in a muffle. It is then roasted, and the sulphur and arsenic expelled as oxides, the latter being condensed in chambers through which the fumes are passed. The roasting must be discontinued when only sufficient arsenic is left to combine with the less oxidisable metals, especially copper and nickel, while the greater part of the cobalt is converted into oxide. In order to ascertain whether the roasting has proceeded sufficiently, a small portion is occasionally tested and the process stopped when the

finest tinted glass is produced. The material is then ready for fusion for 'smalt.'

The fluxes used consist of powdered quartz and potassium carbonate. They must be of great purity, as the presence of lime and many other substances impairs the beauty of the colour. The quartz is first heated to redness, plunged into water, and, thus disintegrated, is powdered in a mill. It is then suspended in water and allowed to subside for a short time, and the liquid, which contains most of the iron and other impurities still suspended, is poured off; this operation is repeated until a pure quartz powder is obtained.

The proportions of the ingredients used vary extremely according to the richness of the ore and the colour required. The potassium carbonate used generally amounts to about one-third of the weight of ore and quartz together. White arsenic is usually added to oxidise any ferrous-salt, and thus prevent the injurious effect of that substance on the smalt, and to otherwise heighten the colour of the product. The exact amount of each of these substances is found by a test fusion and comparison with a smalt of the required colour.

The smalt furnace is similar to a glass oven; it usually contains eight crucibles. The pots are of very refractory clay, free from lime, and capable of holding ¾ cwt. When charged, they are strongly heated, and the mass fuses in about 8 hours; it is frequently stirred to render it homogeneous, and to break the crust which forms on the surface. At a white heat combination occurs, the quartz and potash react with the production of fusible potassium silicate, which dissolves the cobalt oxide, forming the blue 'smalt,' while the mixed arsenides of nickel, copper, and iron, with the small quantity of cobalt arsenide which is always present, fuse and form a brittle metallic-looking *speiss* beneath the smalt. This usually contains about 3 p.c. of cobalt and a considerable quantity of nickel, and is used for the preparation of the latter substance and of cobalt oxide. The mass is left at a white heat for some time without stirring, to allow the speiss to settle, and is ladled out with long-handled iron ladles into vessels of cold water. It is thus rendered granular, brittle, and easy to pulverise. When nearing the bottom of the crucible, the ladle contains both speiss and smalt; the former, being much more fusible, is poured first from the ladle, from beneath the smalt, into a niche in the side of the furnace, whence the dense fumes of arsenic, &c., which it evolves pass up the chimney.

The blue glass is next powdered with granite stampers, or ground between granite millstones under water, and the product passed through a series of depositing vats. In the first vat it remains for a short time only, thence it passes to a second for a somewhat longer time, to a third for about 15 minutes, to a fourth and fifth for a corresponding period, and finally to a sixth vat, where it is allowed to deposit completely. The deposit in the first vat is returned to the mill and reground, that in the second and third is the best marketable smalt, whilst in the fourth and fifth vats a lighter-coloured deposit, sold under the name *eschel*, is produced. The deposit in the last vat is not marketable, and is usually resmelted.

The marketable deposits are again washed, deposited, dried, powdered, and sifted. About three-fifths of the glass taken from the pots is thus available. The presence of other oxides than those of cobalt and potash, even in small quantities, exerts a powerful influence on the colour of the smalt. Baryta produces an indigo tinge; sodium, calcium, and magnesium produce a reddish shade; iron, a blackish green, very prejudicial to the brighter-coloured smalts; manganese violet, nickel violet, but less intense; copper, zinc, bismuth, and antimony, dull shades.

The composition of smalt varies considerably; the silica is usually from 56–70 p.c.; potash, 12–22 p.c.; and cobalt, 6–16 p.c. The following analyses by Ludwig (J. pr. Chem. 1850, 51, 129) are typical:—

—	Norwegian deep-coloured smalt	German deep-coloured	German pale coarse
Silica . .	70·86	66·20	72·12
Potash and soda	21·41	16·31	20·04
Cobaltous oxide .	6·49	6·75	1·95
Alumina . .	0·43	8·64	1·80
Ferrous oxide .	0·24	1·36	1·40
Arsenious acid .	trace	—	0·08
Water and carbonic acid .	0·57	0·92	0·46
	100·00	101·18	97·85

Smalt is a very permanent blue pigment, largely employed for the production of blue colours with vitreous substances and in painting, both for delicate and coarse work. It was formerly much used for colouring starch, paper, &c., but for this and many other purposes it is now almost superseded by the far less permanent artificial ultramarine.

Cobalt yellow consists of potassium cobaltinitrite, prepared by the addition of potassium nitrite to a solution of a cobalt salt acidulated with acetic acid. Its composition varies with the proportions used and the strength of the solution. Erdmann and Sadtler state that when precipitated from a solution containing much acetic acid it consists of $K_3Co(NO_2)_6$ with a variable amount of water.

Cobalt yellow is a bright yellow crystalline powder, very free from impurities, unacted upon by cold water or cold acids, and but slowly blackened by sulphuretted hydrogen.

It forms a fine pigment for artistic purposes. When used for painting porcelain it produces the usual blue colour on baking, which, on account of the purity of the substance, is of great beauty.

Salts of cobalt. The soluble salts of cobalt are prepared by solution of the oxide, carbonate, or metal in the various acids. They are generally pink and deliquescent, forming pink solutions when dilute, but when dried, or in concentrated solution, they are blue. For this reason, solutions of nitrate and other salts of cobalt are used as sympathetic inks, such writing being almost invisible until brought near a fire, when the letters appear blue. They gradually reabsorb moisture and again become invisible. They are largely used for neutralising the

yellow colour of porcelain, and giving a pure white body, the porous clay being for this purpose soaked in solution of cobalt salts.

When ammonia is added to a solution of a cobalt salt, oxygen is absorbed, giving rise under various conditions to many complex series of salts containing ammonia and different oxides of cobalt.

Cobaltous chloride $CoCl_2$ is prepared by dissolving the oxide or carbonate in hydrochloric acid, and evaporating the solution. According to the temperature at which it crystallises, it may contain 6, 4, or 2 molecules of water of crystallisation, the latter at the higher temperatures.

Cobaltous chloride is soluble in water or alcohol. A strong solution, or a weaker solution containing strong hydrochloric acid, is of a blue colour.

Cobaltous sulphate $CoSO_4,7H_2O$ is prepared by solution of the oxide or carbonate in dilute sulphuric acid. It crystallises in red crystals, isomorphous with magnesium sulphate, soluble in 24 parts of cold water.

Cobaltous nitrate $Co(NO_3)_2.6H_2O$ is a red deliquescent crystalline salt prepared by dissolving the oxide in nitric acid. It is very soluble in water, the solution being used as a reagent in blowpipe analysis.

COBALT BLOOM. *Erythrite*; *Hydrated cobalt arsenate* (*v.* COBALT).

COBALT BLUE or **THENARD'S BLUE** *v.* COBALT.

COBALT BRONZE *v.* COBALT.

COBALT CARBONYLS. Cobalt forms two carbonyls: the *tetracarbonyl* $Co(CO)_4$, and the *tricarbonyl* $Co(CO)_3$.

Cobalt tetracarbonyl. This compound is prepared as follows: Cobalt oxalate is carefully heated until completely converted into the oxide. It is then washed free from traces of chlorides which hinder the formation of the carbonyl, and dried at 120°. The oxide is placed in the apparatus described under 'carbonyls,' and reduced to cobalt by means of hydrogen, at a temperature of 300° and a pressure of 5 atmospheres. After the reduction, the hydrogen is displaced by carbon monoxide, the pressure being increased and the temperature lowered. For the production of the carbonyl, a minimum pressure of 40 atmospheres and a temperature of 150° is needed, and at pressures up to 250 atmospheres and temperatures between 150° and 250°, varying quantities of the carbonyl are collected in a tube attached to the outlet of the apparatus, and immersed in a freezing mixture.

The tetracarbonyl forms orange-coloured crystals of sp.gr. 1·73, which melt at 51°, and decompose above that temperature.

The molecular formula is $Co_2(CO)_8$. The compound is insoluble in water, but is soluble in most organic solvents, and in nickel tetracarbonyl. It is not attacked by aqueous acids but concentrated acids and the halogens decompose it, forming the corresponding salt, carbon monoxide, and hydrogen

$$Co(CO)_4+H_2SO_4=CoSO_4+4CO+H_2$$

In contact with air a deep violet-coloured compound is formed, which is most probably a hydrated basic carbonate. The crystals are best preserved in a sealed tube in an atmosphere of hydrogen or carbon monoxide.

When the tetracarbonyl is heated at 60°, one quarter of the carbon monoxide is evolved at a regularly decreasing rate, leaving a compound having the formula $Co(CO)_3$ in the form of black crystals, which are decomposed above 60° into cobalt and carbon monoxide, no intermediate product being formed.

When the tetracarbonyl is heated at 100°, one quarter of the carbon monoxide is evolved almost instantaneously, the rest coming off very irregularly and comparatively slowly (Mond, Kirby, and Cowap, Chem. Soc. Trans. 1910, 97, 798).

COBALT GLANCE. *Grey cobalt*; *Cobaltine*; *Sulpharsenide of cobalt* (*v.* COBALT).

COBALT GREEN or **RINMANN'S GREEN** *v.* COBALT.

COBALT PYRITES *v.* COBALT.

COBALT SPEISS *v.* COBALT.

COBALT ULTRAMARINE or **COBALT BLUE** *v.* COBALT.

COBALT YELLOW *v.* COBALT.

COBALTINE *v.* COBALT.

COCAÏNE *v.* VEGETO-ALKALOIDS.

COCATANNIC ACID *v.* TANNINS.

COCCINE *v.* AZO- COLOURING MATTERS.

α-**COCCINIC ACID, COCCININ,** *v.* COCHINEAL.

COCCULUS INDICUS or **INDIAN BERRY** is the fruit of the *Anamirta paniculata* (Colebar), [*A. Cocculus* (Wight and Arnott)] nat. ord. *Menispermaceæ*, a tree growing upon the coasts of Malabar, Ceylon, &c. The berry is about the size of a large pea and of a dark-grey colour. It possesses strong poisonous and narcotic qualities from the fact of its containing about one-fiftieth part of its weight of picrotoxin, and has been employed to increase the bitterness as also the inebriating effect of beer. It is, however, exceedingly deleterious to health, and the use of it for this purpose has been prohibited by the Legislature under heavy penalties.

Besides picrotoxin, Schmidt and Löwenhardt (Bull. Soc. chim. 14, 817) obtained from the seeds *cocculin* $C_{19}H_{26}O_{10}$, crystallising in white needles, sparingly soluble in hot water, insoluble in cold water, alcohol and ether. It is probably identical with Barth and Kretschy's *anamirtin* $C_{19}H_{24}O_{10}$ which they regarded as a constitutent of picrotoxin.

Cocculus indicus berries contain *menispermine*, *paramenispermine*, and *picrotoxin* (*v.* PICROTOXIN).

COCCUS CACTI, C. ILICIS, C. LACCAL, *v.* COCHINEAL.

COCHIN CHINA WAX *v.* WAXES.

COCHINEAL. This important natural dyestuff, which, in its native country, Mexico, was used as a dye and cultivated by artificial means at a remote period of history, was for a long time considered to be of vegetable origin. Cochineal, however, consists of the dried body of an insect, the *Coccus cacti*, which lives upon a species of cactus (the *Napalea coccinellifera* (S.-Dyck) or *Nopal*), a plant which is found in the wild condition, but which, for the sake of the insect, is cultivated in gardens which are termed *Nopaleries*. The collection of the insects takes place before the commencement of the rainy season, and they are then brushed either into straw baskets or into basins of tinned iron. A number of insects are left upon each plant, and a new generation is produced, which is again gathered at a suitable

period. The insects are killed by immersion in boiling water, or are enclosed in a linen bag and placed in an oven; by the latter process the peculiar white down covering the insect is preserved, but in the former case is lost.

In Mexico and Central America two varieties of cochineal are known—the home-grown, or fine cochineal (*grana fina*); and the wild, or forest cochineal (*grana silvestra*). The former is more valuable than the latter, and is richer in colouring matter. Since 1830 the cultivation of cochineal was introduced into Spain and the Canary Islands, Algeria, and Java, but the most productive of these newer plantations were those of Java. Since the discovery of the coal-tar colours, the consumption of cochineal as a dyestuff has gradually decreased, and at the present time it is only employed in a minor degree. According to Liebermann, cochineal contains about 10 p.c. of colouring matter (Ber. 18, 1969).

Carminic acid, the colouring matter of cochineal, was first isolated by Pelletier and Caventou (Ann. Chim. Phys. [2] 8, 250), and was subsequently examined by Preisser (Annalen, 52, 375; J. Pharm. Chim. [3] 5, 191); and Arppe (Annalen, 55, 101); but Warren de la Rue (*ibid.* 64, 1) was the first to isolate this substance in a pure condition, and described it as a purple-brown mass, which, on grinding, yields a bright-red powder, easily soluble in water and alcohol, but not in ether. The mean of his analyses gave 54·13 p.c. of carbon, 4·62 p.c. of hydrogen, and 41·25 p.c. of oxygen by difference; and from these figures he deduced the formula $C_{14}H_7O_8$ or $(C_{14}H_7O_8)_2$.

Schützenberger (Ann. Chim. Phys. [3] 54, 52), on the other hand, was the first chemist who succeeded in obtaining carminic acid in a crystalline condition. He precipitated the colouring matter from an aqueous cochineal extract in the form of its lead compound; suspended this in water, and decomposed it with sulphuretted hydrogen. The liberated carminic acid dissolved in the water and was recovered from this solution by evaporation at a low temperature. The product, dissolved in alcohol, was treated with ether to precipitate certain impurities, and the liquid partially evaporated. On cooling, a crystalline mass was obtained, which Schützenberger considered to consist of two substances, carminic acid $C_9H_8O_5$, and oxycarminic acid $C_9H_5O_6$, the latter being distinguished by its solubility in ether.

Schaller (J. 1864, 410), who prepared carminic acid by the same method, assigned to it, however, the formula $C_9H_9O_6$.

The work of Hlaziwetz and Grabowski (Annalen, 141, 329) indicated that carminic acid was a glucoside which could be decomposed into a sugar and a new colouring matter, *carmine red*:

$$\underset{\text{Carminic acid.}}{C_{17}H_{18}O_{10}} + 2H_2O = \underset{\text{Carmine red.}}{C_{11}H_{12}O_7} + \underset{\text{Sugar.}}{C_6H_{10}O_5}$$

but according to Liebermann (Ber. 18, 1969; Will and Leymann, *ibid.* 18, 3182; and Von Miller and Rohde, *ibid.* 26, 2647), this is incorrect.

Coccinin, according to Hlaziwetz and Grabowski, is produced when carminic acid is fused with caustic potash. It crystallises from alcohol in straw-yellow needles or leaflets, dissolves in alkalis with a yellow colour, which, by air oxidation, develops first a green then violet, and, finally, a purple tint. The analyses of this substance were in agreement with the formula $C_{14}H_{12}O_5$.

Ruficoccin.—By heating carminic acid with sulphuric acid to 130°–140°, Liebermann and van Dorp (Annalen, 163, 105) obtained a new colouring matter ruficoccin, $C_{16}H_{10}O_6$, and this consisted of a bright-red powder, sparingly soluble in hot water and ether, with a greenish-yellow fluorescence. On distillation with zinc-dust, it yielded a colourless crystalline hydrocarbon $C_{16}H_{12}$, m.p. 183°–188°, from which, by oxidation, a quinone melting at 250° could be produced.

Fürth, somewhat later (Ber. 16, 2169), prepared the same hydrocarbon by the distillation of both cochineal carmine and coccinin with zinc-dust.

Ruficarmine $C_{16}H_{12}O_6$ can be obtained, according to Liebermann and van Dorp, by heating carminic acid with water in a sealed tube at 200°. It consists of a carmine-red powder, easily soluble in alcohol.

In view of the uncertainty existing as to the percentage composition of carminic acid, Schunck and Marchlewski (Ber. 27, 2980) submitted this substance to an elaborate process of purification, and, using in their operations as low a temperature as possible, obtained a product which crystallised from alcohol in red prismatic needles. Their analysis agreed closely with that required by the formula $C_{11}H_{12}O_6$, and the percentage composition approximated with the figures given by Warren de la Rue, and also by Schützenberger.

On the other hand, analyses by Miller and Rohde (Ber. 30, 1762) indicated the formula $C_{12}H_{11}O_7$ or $(C_{12}H_{11}O_7)_2$ as probable; but it now appears, according to the more recent work of Liebermann, Höring, and Wiedermann (Ber. 1900, 33, 149), that the correct formula of carminic acid is $C_{22}H_{22}O_{13}$.

The most simple method for the purification of carminic acid is that devised by Miller and Rohde. A solution of the crude colouring matter in five times its weight of water, is diluted with four times its volume of acetic acid. The filtered liquid, on standing over sulphuric acid, gradually deposits the carminic acid in a crystalline condition.

Carminic acid crystallises in red prisms, easily soluble in water and alcohol, with a purple-red colour. It possesses no melting-point, but darkens at 130°, and at 250° becomes quite black-coloured.

By the action of alcoholic potassium acetate, carminic acid (Perkin and Wilson, Chem. Soc. Trans. 1903, 83, 139) yields two potassium salts, viz.:

Monopotassium carminate $C_{22}H_{23}O_{13}K$ (probably $C_{22}H_{21}O_{13}K$) which is red-coloured; and

Dipotassium carminate $C_{11}H_{11}O_6K$ (probably $C_{22}H_{20}O_{13}K_2$) soluble in water, with a violet-red colouration.

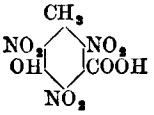
Hexabenzoyl carminic acid $C_{22}H_{16}O_{13}(C_7H_5O)_6$, obtained by digesting carminic acid with benzoyl chloride (Liebermann, Höring, and Wiedermann) is an orange-coloured powder, easily soluble in benzene.

Octacetyl carminic acid $C_{24}H_{12}O_{13}(COCH_3)_8$? (probably $C_{22}H_{14}O_{13}(C_2H_3O)_8$) crystallises in golden-yellow needles, m.p. 155°–165°, and is

readily prepared by the short action of acetic anhydride in presence of zinc chloride or sulphuric acid on carminic acid (Miller and Rohde).

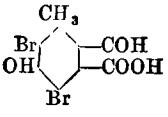
THE CONSTITUTION OF CARMINIC ACID.

Nitrococcissic acid was obtained by W. de la Rue from carminic acid by the prolonged action of boiling nitric acid. It was subsequently studied by v. Kostanecki and Niementowski (Ber. 18, 250), and was found to be identical with the *trinitrocresotinic acid*, of the following constitution :—

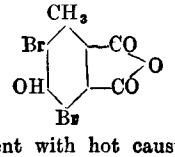


When carminic acid dissolved in 50 p.c. acetic acid is treated with an excess of bromine, and the solution digested at the boiling heat, two substances, known as α- and β-bromcarmines, are produced (Will and Leymann, Ber. 18, 3180).

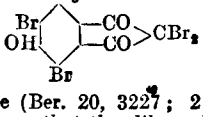
α-Bromcarmine $C_{10}H_4Br_4O_5$, the more sparingly soluble substance, crystallises in colourless needles, and melts at 247°–248°, with decomposition. When oxidised with potassium permanganate in alkaline solution, it gives *dibrommethylhydroxyaldehydobenzoic acid*,



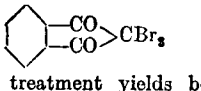
and *dibrommethylhydroxyphthalic anhydride*



On treatment with hot caustic soda solution, α-bromcarmine yields, in addition to a purple-red colouring matter, dibrommethylhydroxyphthalic acid, and bromoform (Miller and Rohde). As a result of this reaction, these authors assigned to α-bromcarmine the constitution of a methylhydroxytetrabromdiketohydrindene

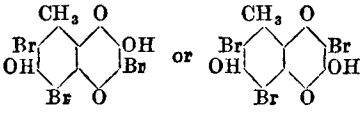


For Zincke (Ber. 20, 3227; 21, 2388) had previously shown that the dibromdiketohydrindene itself

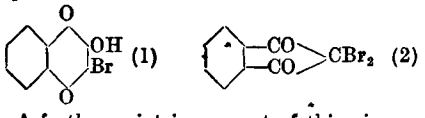


under similar treatment yields both phthalic acid and bromoform.

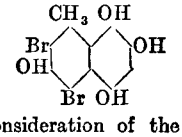
β-Bromcarmine $C_{11}H_5Br_3O_4$ is obtained as a yellow amorphous powder, easily soluble in alcohol (Will and Leymann), and is best purified by means of its potassium salt. Crystallised from acetone, it separates in orange needles, melting at 232° (W. and L.) or 288° (Miller and Rohde). By the action of bromine in the presence of 50 p.c. acetic acid solution, it is converted into α-bromcarmine. As a result of their investigation, Miller and Rohde ascribed to β-bromcarmine the constitution of a *methyldihydroxytribrom-a-naphthaquinone*, possessing one of the following formulæ :—



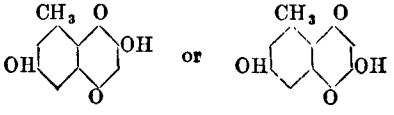
This suggestion was supported by the fact that bromoxynaphthaquinone (1), on treatment with bromine and caustic soda solution, is converted into dibromdiketohydrindene (2) (Zincke, *l.c.*)



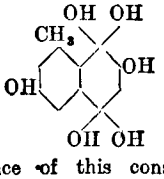
A further point in support of this view was obtained by a study of the behaviour of β-bromcarmine with zinc-dust in alcoholic solution. Thus the acetyl compound of the reduction product, m.p. 206°, gave, on analysis, numbers agreeing with those of the acetyl derivative of a *methyldibromdihydroxynaphthahydroquinone*, possessing the following formula :—



From a consideration of the points above enumerated, Miller and Rohde considered that the constitution of carminic acid could be represented by one or other of the following expressions :—



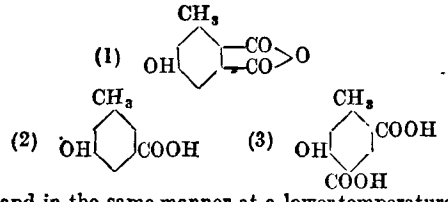
As, however, such formulæ require C=64·7 p.c., H=3·92 p.c., figures which are much higher than those given by the analysis of carminic acid itself, these authors suggested the addition of two molecules of water of hydration, as shown below :



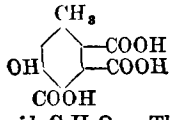
A substance of this constitution would require C = 55 p.c., and H = 5 p.c.

Somewhat later, Liebermann and Voswinkel (Ber. 30, 688) studied the oxidation of carminic acid with alkaline potassium permanganate at the ordinary temperature, and in this way succeeded in producing two important acids.

Cochinealic acid $C_{10}H_8O_7$ crystallises in colourless needles, which melt at 224°–225° with evolution of CO_2. It is tribasic, at 260° is converted into *hydroxymethylphthalic anhydride* (1); when heated with water in a sealed tube at 210° yields symmetrical *cresotinic acid* (2)

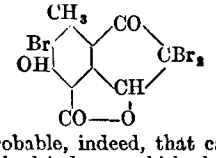


and in the same manner at a lower temperature, 170°, gives *α-coccinic acid* (3). The constitution of cochinealic acid was therefore as follows:—

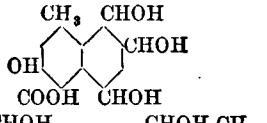


α-Coccinic acid $C_9H_8O_5$. The second product of the oxidation, which, as already indicated, can also be prepared from cochinealic acid, proved to be identical with the hydroxyuvitinic acid of Oppenheim and Pfaff (Ber. 7, 929). It consists of colourless needles, m.p. 239°.

Liebermann (*ibid.* 30, 1731), whilst agreeing with the diketohydrindene constitution which had been assigned to *α*-bromcarmine by Miller and Rohde, considered that *β*-bromcarmine was an indone rather than a naphthoquinone derivative, and could be better represented as follows:—



It was probable, indeed, that carminic acid itself was a hydrindene or bishydrindene derivative, and the following constitutions were suggested for it:—



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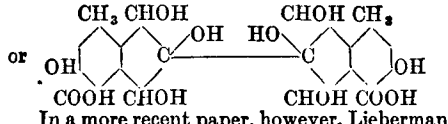
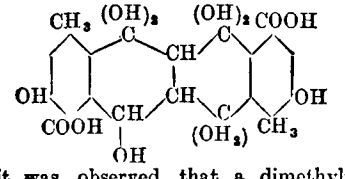
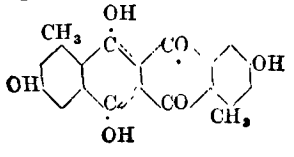


In a more recent paper, however, Liebermann and Voswinkel (Ber. 37, 3344) consider that carminic acid is possibly a *tetrahydrate of α-dimethyldihydroxynaphthacenequinonedicarboxylic acid*



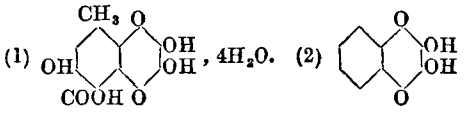
and it was observed that a dimethyltetrahydroxynaphthacenequinone



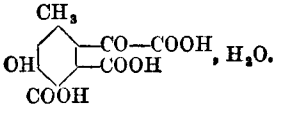
prepared by these authors not only possessed weak tinctorial property of a cochineal-like character, but in several respects closely resembled carminic acid itself.

A valuable contribution to the subject was made by Dimroth (Ber. 1909, 42, 1611) who studied the oxidation of carminic acid with potassium permanganate at 0° in presence of sulphuric acid. The solution thus obtained gave nothing to ether, but on heating for three-quarters of an hour at 90°, it evolved carbon dioxide, and ether then extracted carminazarin.

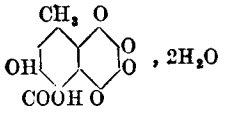
Carminazarin crystallises from water in garnet-red needles, decomposing at 240°–250°. It possesses the constitution (1), and is very similar to *iso*naphthazarin (2).



Its alkaline solution, when treated with a stream of oxygen, is quickly decolourised with formation of *5·6-dicarboxy-4-hydroxy-o-tolylglyoxylic acid*

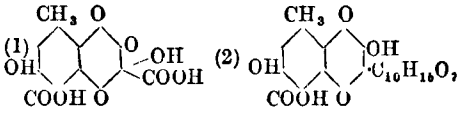


A further point of resemblance of carminazarine to *iso*naphthazarine is shown by its behaviour with nitric acid in glacial acetic acid, for whereas the latter gives tetraketotetrahydronaphthalene, the former yields the analogous *Carminazarinquinone* crystallising in colourless prisms,

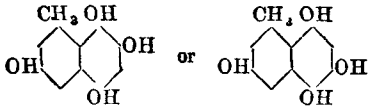


and which, when heated with water or acetic acid, passes back to carminazarin.

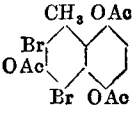
The intermediate product formed by the oxidation of carminic acid with permanganate at 0°, and which, on heating, is transformed into carminazarin, is termed by Dimroth *carminoquinone*. The constitutions assigned to this substance (1) and to carminic acid (2) are given below:—



Carminic acid is, therefore, not a symmetrical compound, and the nature of the group $C_{10}H_{11}O_7$ has not yet been determined. Finally, it is considered by Dimroth that the *coccinin* (*see* above) of Hlaziwetz and Grabowski, and which is prepared by fusing carminic acid with potassium hydrate, has probably the constitution of a *tetrahydroxymethylnaphthalene*.

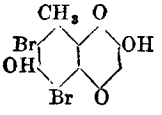


Rohde and Dorfmüller (Ber. 1910 33, 1363) further examined β-bromcarmine, and obtained results which support the naphthaquinone constitution assigned to it by Miller and Rohde (*l.c.*), but disprove Liebermann's contention that it is a derivative of indone. By reduction with zinc-dust and acetic acid and subsequent acetylation, β-bromcarmine gives the compound $C_{17}H_{14}O_6Br_2$;



colourless needles; m.p. 208°.

Simultaneous hydrolysis and oxidation converts this into the substance



orange prisms; m.p. 258°; and it thus appears that by the latter treatment an hydroxyl has probably entered the quinone nucleus. The diacetyl derivative melts at 233°. When distilled with zinc-dust, this product, and also β-bromcarmine itself, give naphthalene.

Technical Preparations of Cochineal.

Ammoniacal cochineal.—When a solution of carminic acid in ammonia is allowed to stand for some time, there is formed a new compound, which appears to consist of carminic acid in which one of the hydroxyls has been replaced by an amino- group. The formula assigned to this substance by Schützenberger is $C_9H_9NO_4$. This reaction, long known, has been utilised for the production of a new colouring matter termed *ammoniacal cochineal*, or *carminamide*, and this comes into commerce either as cakes or in the form of a paste.

The first variety is usually prepared by allowing one part of cochineal to stand in a closed vessel for 3 months with three parts of ammonia. The clear liquid is decanted, treated with about half its weight of gelatinous alumina, evaporated, and, when the mass has become thick, it is cut up into cakes and dried.

The paste is manufactured in a somewhat similar manner, the ammonia, however, being only allowed to react for 8 days. The clear liquid is then evaporated to about one-third its bulk without addition of alumina (Crookes, Dyeing and Calico Printing).

Ammoniacal cochineal dyes much bluer shades than cochineal itself, and is sometimes employed in conjunction with the latter. Its use is now very limited, but it finds some application in the blueing of bleached cotton.

Cochineal carmine (*see* under Lakes).

Dyeing Properties of Cochineal.

Cochineal has been little employed in cotton dyeing, but was very largely used in silk dyeing and wool dyeing. It has now been practically replaced by the azo- scarlets.

Two shades of red are obtained upon wool with cochineal, namely, *crimson*, which is produced by means of aluminium sulphate, and a very fiery *scarlet*, for which stannous and sometimes stannic chloride are employed.

For crimson, wool is mordanted with aluminium sulphate and tartar, and is then dyed in a separate bath with cochineal. The employment of calcium salts in the dyeing operation is not beneficial. Fairly good shades of crimson can also be obtained by mordanting and dyeing in a single bath with aluminium sulphate, oxalic acid, and cochineal. For scarlet, wool can be mordanted with stannous chloride and tartar, and dyed in a separate bath with cochineal. A single-bath method, employing stannous chloride, oxalic acid, and cochineal, has, however, been very largely employed for this purpose. On the other hand, preparations of stannic chloride, known as 'tin spirits,' 'scarlet spirits,' and 'nitrate of tin,' are and have been much employed by dyers of cochineal scarlet. Though, when used alone, stannic chloride does not give such brilliant shades as the stannous mordant, a mixture of both is considered to be beneficial.

For very yellow shades of scarlet, yellow colouring matters can be added to the cochineal dye-bath, and of these 'flavine' has been considerably employed.

Cochineal red on wool possesses considerable fastness to light, but has the defect that weak alkalis and soap cause it to acquire a duller or more bluish shade.

Wool mordanted with potassium dichromate gives with cochineal a good purple colour, whereas with ferrous sulphate and tartar, purplish slate or lilac colours can be produced. These mordants, however, are not employed in practice.

A good crimson shade is produced by mordanting silk with alum, and dyeing with an extract of cochineal. In scarlet dyeing, silk is preferably first dyed yellow, then mordanted with 'nitromuriate of tin,' and finally dyed in a second bath with the assistance of cream of tartar. Silk can also be dyed in a single bath with cochineal, stannous chloride and oxalic acid.

A. G. P.

COCHINEAL CARMINE *v.* Lakes.

COCHINEAL RED, SCARLET *v.* Azo- colouring matters.

COCHINEAL WAX and FAT. The wax is obtained by extracting the cochineal with benzene, and consists almost entirely of a substance to which Liebermann gave the name *coccerin*. After the removal of the coccerin, the fat is extracted with ether; it consists of myristin and an oil containing fatty acids. The following are the percentages of coccerin in various samples of cochineal (extracted whole with benzene):

Silver cochineal . .	1·0 p.c.
Mexican silver cochineal .	1·7 „
Teneriffe silver cochineal .	2·0 „
Zaccatille . . .	0·5 „
Teneriffe black cochineal .	0·7–1·0 „
Mexican black cochineal .	1·5 „
Granilla	4·2 „

By powdering the cochineal before extraction, the percentage is increased by about one-half, except in the case of Granilla, where the granules are exceedingly small. The percentage of myristin is on the average about 1·5–2·0, and of fluid fat and fatty acids 4·0–6·0, so that the average total quantity of wax and fat contained in a silver cochineal is about 12 p.c. After recrystallising from benzene or acetic acid, coccerin forms thin glistening plates of melting-point 106°. It is sparingly soluble in all cold solvents, and nearly insoluble in alcohol and ether. It has the constitution $C_{30}H_{60}(C_{31}H_{61}O_3)_2$. On saponification with alcoholic potash, it gives *cocceryl alcohol* $C_{30}H_{60}(OH)_2$ and *cocceric acid* $C_{31}H_{62}O_3$. The alcohol forms a white crystalline powder of m.p. 101°–104°. The acid melts at 93°, and is soluble in hot alcohol, benzene, &c.; its ethyl ether melts at about 70°. The myristin $C_3H_5(OC_{14}H_{27}O)_3$ forms colourless crystals of m.p. 55°, easily soluble in warm alcohol, &c.; on saponification it gives glycerol and myristic acid $C_{14}H_{28}O_2$ of m.p. 54°, and b.p. 248° at 100 mm. (J. Soc. Chem. Ind. 4, 585).

COCHINEALIC ACID *v.* COCHINEAL.

COCINIC ACID *v.* HENDECATOIC ACIDS.

COCOA. The cocoa tree is an evergreen shrub, indigenous to Mexico and the tropical regions of Central America, whence it was introduced into Europe by the Spaniards. It belongs to the natural order *Sterculiaceæ*, and comprises several species, that most highly valued and cultivated being the *Theobroma cacao*, so called by Linnæus, from *θεός* (god) and *βρῶμα* (food), in allusion to the esteem and almost veneration in which the beverage prepared from its seeds was held by the natives of Central America, and 'cacao,' the name by which it was originally known. The seeds were used as a kind of money even down to the time of Humboldt's visit to Mexico.

The tree grows to a height of from 12 to 40 feet, the average being about 25 feet, but in plantations it rarely exceeds 18 feet. It flourishes best in a moist and warm climate, in latitudes between 25° north or south of the equator, and at altitudes up to 1000 feet. It is now cultivated more or less extensively in Brazil, Caraccas, Central America, Ecuador, Essiquibo, Grenada, Guayaquil, Peru, Trinidad, Venezuela, and in the West Indies (particularly Jamaica, Dominica, and St. Lucia); also in Ceylon, the East Indies, the Philippines, Mauritius, Madagascar, San Thomé, Gold Coast, Cameroons, and to some extent in Australia.

The cocoa tree begins to bear fruit when 3 years old, and attains its full productiveness when 7 or 8 years old, but a healthy tree will bear for 40 or 50 years. Fruit is produced all the year round, but harvesting usually takes place only twice a year—from February to April, and again in October and November.

The fruit consists of an elongated pod, in shape between a melon and a cucumber, measuring from 5 to 12 inches in length, and from 2 to 4 inches in diameter, with a thick pericarp varying in colour from yellow or red to purple, according to the variety. There are from 20 to 40 or more seeds in a pod (though the number is smaller in the West Indian varieties) arranged in 5 longitudinal rows, and embedded in a rose-coloured mucilaginous pulp. When fresh they are usually white (some varieties purple), and have a bitter taste, but after drying and exposure to the air and light they acquire a yellow, red, or brown colour, and become hard, brittle, and less bitter. They are ovate, compressed, and about the size and shape of haricot beans or olives.

After removal from the pods, the seeds or beans are either freed at once from adhering pulp and dried in the sun (or occasionally by artificial means), to produce 'unfermented cocoa,' or they are removed to the 'sweating' or curing house to undergo a process of fermentation before drying. Unfermented cocoa is distinguished by its pale skin, which separates with difficulty from the kernel. Owing to its bitter taste, it is suitable only for use in cocoa mixtures containing starch and sugar. It is quite unfit for chocolate making, and commands a lower price than fermented cocoa.

To produce fermented cocoa, the beans were formerly buried in the ground, or in trenches covered with plantain leaves, but in order to avoid the consequent adherence of earthy matter, they are now generally buried in casks or boxes, or heated in piles in sheds, and turned over once or twice daily. The temperature rises considerably during fermentation, and the process requires great care and skill, as on it the commercial value of the finished beans chiefly depends.

The objects arrived at in the 'sweating' operations are the loosening of the adherent pulp, the removal or modification of the bitter principle, the development of an agreeable aromatic odour, and the colouration of the beans to a rich mahogany tint. The fermentation process generally lasts from 2 to 7 days. In some parts, as Trinidad and Jamaica, red earth is often employed to assist in the removal of the mucilage from the beans, which are afterwards rubbed clean and dried. Occasionally Venetian red is used to impart a uniform red tint to the finished beans.

In the drying operation the beans are spread out in trays and systematically turned so as to expose every part of the bean to the light, and, when thoroughly air-dried, are in a suitable condition for shipment.

The preliminary processes of manufacture consist in (*a*) *sifting* out sand, dust, and small stones; (*b*) *picking* out by hand the empty beans and foreign matter, as larger stones, grass, wood &c.; (*c*) *roasting*; and (*d*) *cleaning*, by breaking up the beans and removal of the husks or shells. Berhardt (Chem. Zeit. 1889, 32) has found, from the results of actual factory work, that the losses in these operations amount to 2 or 3 p.c. in sifting; nearly 1 p.c. in picking; about 5 p.c. in roasting; and 12 or 13 p.c. in cleaning; making a total loss of over 20 p.c.

The roasting process, which requires great care, skill, and experience on the part of the operatives entrusted with it, is conducted in rotating cylinders heated by coke fires or by means of superheated steam in pipes lining the cylinders, to a temperature varying from 500° to 600°F. (260° to 315°C.). Uniformity of roasting is facilitated by grading the beans in the same operation to a uniform size. The beans are then cooled, gently crushed in a 'kibbling mill,' to fracture the crisp husk and break down the kernel into its natural angular

fragments or 'nibs,' after which the nibs, husks, and hard rod-shaped germs are separated by winnowing and sieving, and the nibs graded into different classes according to size.

The object of roasting is to develop to the fullest extent the characteristic aroma and flavour of the cocoa. This is probably due to the development of a volatile principle in the nature of an essential oil, somewhat analogous to the caffeol of coffee (*v. infra, Cocoa-red*).

The roasted husks or shells constitute on an average about 12 or 13 p.c. of the weight of the whole bean, varying from 7 or 8 p.c. in the thin-walled beans of Ceylon and Java to 18 p.c. in those of Trinidad and the West Indies, which have a much thicker shell. The shells form a low-priced product extensively used, after grinding, in the cheaper grades of cocoa and chocolate, and occasionally, under the name of 'cocoa tea,' as a beverage which has the taste and flavour of weak cocoa. Cocoa shells have proved to be a useful addition to feeding stuffs, especially for milch cows, and gave good results on the experimental farms of Canada when used as manure. (For analysis of cocoa shells, *see* table below.)

The nibs enter into commerce as such, but although in this form the consumer may be assured of the purity of the article, yet, owing to the large proportion of fat in them (about half their weight) and the difficulty of dis-integrating them even by boiling water, they are hardly suitable for popular use as a beverage.

For the manufacture of the various forms of prepared cocoa, the nibs are ground by means of millstones or steel mills so constructed as gradually to reduce the cocoa to the finest and smoothest possible condition. If the cocoa is to go into consumption as ground nibs in powder, the stones or rollers are kept cool during the operation, but if, as is usual, the ground cocoa is afterwards to be made up into any of the numerous forms of prepared cocoa or chocolate, the stones or rollers are usually kept heated during the grinding. This causes the fat to melt, and the whole is reduced to a liquid mass, which is run into moulds and cooled so as to form blocks, which are sold as such or kept as stock for subsequent conversion into prepared cocoa or chocolate.

The leading types of manufactured cocoa are *flake cocoa, rock cocoa,* and cocoa powders sold under such names as 'soluble' cocoa, and 'extract' or 'essence' of cocoa. *Flake cocoa* is prepared simply by grinding the whole beans or the nibs only in steel mills somewhat resembling those used for grinding coffee. *Rock cocoa* is made in the form of a paste by grinding in a mill with heated stones or rollers, and with the addition of sugar and starch.

The admixture of starch or other gelatinising substance tends to mask the presence of the fat and to render the cocoa more readily miscible with boiling water. These mixtures, sold under such names as 'homœopathic,' 'Iceland moss,' &c., are frequently described as 'soluble cocoa,' but this is a misnomer, since the absence of a sediment in the cup is due, not to solution of the cocoa, but to the formation of an emulsion, which holds the cocoa in a finely divided state suspended in the liquid. In some of these, as 'granulated cocoa,' 'cocoatine,' &c., sugar is added as well as starch.

The large proportion of fat (about 50 p.c.), being found by many to be difficult of digestion, is reduced in preparations intended for use as a beverage, not only by the addition of sugar and starch (which incidentally reduces the proportion of cocoa present), but also by the actual abstraction of fat to form the so-called 'essence' or 'extract' of cocoa.

The partial extraction of the fat is accomplished by submitting the pure cocoa paste enclosed in strong canvas bags to a pressure of 1200-1400 lbs. per square inch in hydraulic presses heated to 70°-80°. The cocoa butter flows out through a special orifice, and is afterwards solidified into blocks or slabs ready for use in surgical and pharmaceutical preparations, for soap making, and in the manufacture of chocolate confectionery. The commercial value of cocoa butter (which is twice that of the raw cocoa) is no doubt an inducement to its removal, in addition to the alleged purpose of making the cocoa more digestible.

To prepare the so-called 'essence' or 'extract' of cocoa, the cakes of compressed cocoa, now containing only about 25 p.c. of fat, are turned out in a nearly dry condition, and ground to a fine powder. Some cocoa powders are said to be rendered more digestible by treatment with alkalis, which soften the cellulose tissue and act upon the fat so as to produce a more perfect emulsion than that obtained by other 'soluble' cocoas prepared with starch; also there is less tendency to separation of the melted fat in the cocoa beverage. Another method is to soften the tissue by heating in closed vessels with or without water to a temperature of 150°. In some preparations, as 'solidified cocoa,' the fat is not removed, whilst a preparation of cocoa practically free from fat is obtained by extracting the roasted and ground beans with ether or benzene. The ordinary flavouring materials are vanilla and cinnamon, but other spices and artificial vanilla are occasionally used.

The principal constituents of cocoa are fat ('cocoa butter'), alkaloids, albuminoids, starch, tannin, cocoa-red, and mineral matter.

ANALYSES OF RAW COCOA NIBS.

	Bell	Boussingault
Moisture	5·23	7·6
Fat	50·44	49·9
Starch	4·20	2·4
Albuminous matter:		
Soluble	6·30	10·9
Insoluble	6·96	
Astringent principle	6·71	0·2
Gum	2·17	2·4
Cellulose	6·40	10·6
Alkaloids	0·84	3·3
Cocoa-red	2·20	—
Indefinite organic matter (insoluble)	5·80	5·3
Ash	2·75	4·0
(Tartaric acid)	—	3·4
	100·00	100·0

The *fat, cocoa butter,* or *cacao butter, oleum theobromæ,* is the principal food constituent of cocoa, and forms from 45–55 p.c. of the husked bean. It has a pleasant taste and odour, suggestive of chocolate. At ordinary temperatures it is a yellowish-white, somewhat brittle solid, melting below the temperature of the body, viz. 28°–33°, and solidifying at 21°–23°; sp.gr. from 0·95 to 0·97 at 15°, and 0·856 at 100°; iodine number from 33 to 38; saponification value, 193–195; refractometer reading (Zeiss) at 40° is 46–47·8; and index of refraction, between 1·4565 and 1·4578 at 40°. It is readily soluble in ether, chloroform, turpentine, and boiling alcohol, from which it crystallises out almost completely on cooling. Chemically, it is a mixture of the glycerides of stearic, palmitic, oleic, and arachidic acids (Benedikt, Analyse der Fette und Wachsarten). It is sometimes adulterated with such substances as coco-nut oil, cotton seed, and sesamé oils, stearin, tallow, and paraffin wax. Illipé oil is often used as a substitute for cocoa butter (which it closely resembles in certain respects) in the manufacture of chocolate.

Alkaloids.—Theobromine $C_5H_2(CH_3)_2N_4O_2$, or dimethylxanthine, is the principal alkaloid in cocoa, and is closely related to the alkaloid of tea and coffee, caffeine (trimethylxanthine), which is also present to a small extent in cocoa. Theobromine crystallises in white microscopic needles, having a bitter taste, and is present in cocoa to the extent of about 1·5 p.c. The published analyses show variations from 0·4 to 3·3 p.c., due to the different methods of analysis employed. One of the best methods is that of Decker, as modified by Welmans and Fromme (Pharm. Zeit. 47, 798, and 858; and Apoth. Zeit. 18, 68). The caffein is usually included with the theobromine, from which, however, it can readily be separated by means of cold benzene, in which caffeine is soluble, but theobromine practically insoluble. The amount of caffeine varies from 0·1 to 0·3 p.c. (*see* art. THEOBROMINE).

Albuminoids.—These have been but little studied, but Stutzer (Zeitsch. angew. Chem. 1891, 368) has classified the nitrogenous constituents of cocoa as follows:—

(1) Non-proteids, substances soluble in neutral water solution in presence of copper hydroxide (theobromine, ammonia, and amino-compounds).

(2) Digestible albumen, insoluble in neutral water solution in presence of copper hydroxide, but soluble when treated successively with gastric juice and alkaline pancreas extract.

(3) Insoluble and indigestible nitrogenous substances.

According to Stutzer's analyses, the proportion of albuminoids in cocoa powder manufactured without chemicals is between 17 and 18 p.c., of which 10 p.c. is soluble or digestible albumen, the remainder (over 40 p.c. of the whole) consisting of insoluble and indigestible substances. Forster, however, maintains that the proportion of digestible albuminoids reaches as high as 80 p.c., his experiments being made on the human subject, whilst Stutzer's were conducted under laboratory conditions (Hyg. Rundschau, 1900, 314).

Starch, as in oleaginous seeds generally, is not very abundant. It has been variously estimated from 2 to 20 p.c. of the nib, but many of the results are too high, owing, no doubt, to the conversion of cellulose into sugar when the acid method for the starch conversion is employed. The diastase method is preferable in the presence of cellulose. The average amount of starch is from 4 to 5 p.c., or about 8 p.c. calculated on the fat-free bean. The starch grains are nearly spherical, with a very indistinct nucleus. They have a tendency to unite in small groups of 3 or 4, and rapidly lose the colour imparted by iodine. The average size is about 0·005 mm.

Tannin.—An astringent principle resembling tannin exists in the raw bean, but, according to Mitscherlich and Bell, it is rapidly oxidised to 'cocoa-red,' to which the characteristic colour of cocoa is due. Bell (Foods, i. 79) states that this astringent principle is different from the tannin of tea and coffee, and that its rapid change to cocoa-red, even during the process of analysis, renders its quantitative estimation difficult. It is precipitated by basic acetate of lead, and can be obtained after removal of the lead by sulphuretted hydrogen. It gives a green precipitate with ferric chloride not unlike caffeic acid under similar treatment.

Cocoa-red is not present in the fresh seeds, which are nearly white, but arises from the oxidation of the natural tannin of the seed. It consequently appears in different quantities in different kinds of cocoa. On hydrolysis it decomposes into glucose, tannin, and a resinous substance. By many the peculiar taste and aroma of cocoa are associated with the formation of cocoa-red, which increases in amount during the process of fermentation, drying, and roasting, simultaneously with a corresponding increase in flavour, thought to be due to the development of a volatile principle or essential oil. Details of methods for its extraction and estimation are given in Zipperer (Die Schokoladen Fabrikationen) and Blyth (Foods).

Mineral matter. The ash in cocoa nibs varies from 2·5 to 4·5 p.c., the average, according to Zipperer, being 3·6 p.c. in raw, and 3·9 p.c. in the roasted kernels. The shells contain two or three times this amount. Approximately half the ash (which is rich in potash and phosphates) is soluble in water. The ash is naturally lower than the average when starch or sugar has been added, and higher when fat has been abstracted, or when the cocoa has been adulterated with husks or coloured with pigments. The shell is rich in alkaline carbonates and silica as compared with the nib. A high alkalinity in the ash of cocoa powders indicates treatment with alkalis as described in the preparation of the so-called 'soluble' cocoas. The composition of the ash of cocoa nibs and husks is shown in the table given below.

Whilst cocoa ranks higher than tea or coffee as a nutritious beverage, its value as a substitute for solid food has been greatly exaggerated. In its content of alkaloid and tannin substances, it stands midway between tea and coffee, and, like them, it should be considered a stimulating beverage rather than a true food.

The following tables will serve to show the composition of cocoa nibs, shells, the ash, and several kinds of commercial cocoas:—

Composition of Cocoa Shells (Weigmann).

Commercial varieties	Moisture	Nitrogenous substances	Theobromine	Fat	Nitrogen-free extract	Cellulose	Ash	Sand	Total nitrogen
Caraccas . . .	12·49	13·18	0·58	2·38	40·30	16·33	9·06	6·26	2·11
Trinidad . . .	14·64	14·62	0·74	3·45	44·89	15·79	6·19	0·42	2·34
Surinam . . .	13·93	16·25	0·78	2·54	42·47	17·04	6·63	0·85	2·60
Puerto Cabello . .	14·89	16·18	0·75	2·01	43·32	15·25	8·08	0·27	2·59

Roasted Beans after Removal of the Husk (Heisch).

——	Husk	Fat	Nitrogen	Albuminoids	Ash	Ash soluble in water	Ash soluble in HCl	H_3PO_4 in ash	Moisture	Starch, gum cellulose, &c.
Caraccas .	13·8	48·4	1·76	11·14	3·95	2·15	1·80	1·54	4·32	32·19
Trinidad .	15·5	49·4	1·76	11·14	2·80	0·90	1·90	0·93	3·84	32·82
Surinam .	15·5	54·4	1·76	11·14	2·35	0·80	1·85	1·23	3·76	28·35
Guayaquil .	11·5	49·8	2·06	13·03	2·50	1·75	1·75	1·87	4·14	30·47
Grenada .	14·6	45·6	1·96	12·40	2·40	0·60	1·80	1·35	3·90	35·70
Bahia .	9·6	50·3	1·17	7·40	2·60	0·90	1·70	1·26	4·40	35·30
Cuba . .	12·0	45·3	1·37	8·67	2·90	0·95	1·95	1·13	3·72	39·41
Para . .	8·5	54·0	2·00	12·66	3·05	1·40	1·65	1·00	3·96	26·33

Analysis of the Ash of Cocoa Nibs and Husks (Bell).

——	1 Guayaquil nibs	2 Surinam nibs	3 Grenada nibs	4 Finest Trinidad nibs	5 Finest Trinidad husks
Sand	—	—	—	—	5·12
Silica	0·15	—	—	—	2·87
Sodium chloride . . .	0·46	0·53	0·57	0·65	0·44
Soda (Na_2O)	0·46	0·63	0·57	0·83	0·94
Potash (K_2O)	23·35	28·00	27·64	29·30	37·89
Magnesia	19·18	20·66	19·81	18·23	13·04
Lime	3·24	4·38	4·53	6·51	7·30
Alumina	0·10	0·04	0·08	0·08	0·55
Iron oxide (FeO) . . .	0·21	0·38	0·15	0·10	0·63
Carbonic anhydride (CO_2) .	0·69	3·31	2·92	4·19	10·80
Sulphuric „ (SO_3) .	2·77	4·29	4·53	3·91	3·25
Phosphoric „ (P_2O_5) .	49·39	37·78	39·20	36·20	17·17
	100·00	100·00	100·00	100·00	100·00

The following table shows the general composition of commercial cocoas :—

Analysis of Commercial Cocoas (Bell).

——	Prepared cocoa	Iceland moss cocoa	Rock cocoa	Flake cocoa	Cocoatina	Chocolatine	Finest Trinidad nibs	Chocolat de Santé	Cocoa extract
Moisture . .	4·95	5·47	2·58	5·49	3·52	4·40	2·60	1·44	5·76
Fat . .	24·94	16·86	22·76	28·24	23·98	29·60	51·77	22·08	29·50
Starch (added)	19·19	24·70	17·56	none	none	none	none	2·00	none
Sugar (cane) .	23·03	29·23	32·20	none	none	none	none	61·21	none
Non-fatty cocoa	27·89	23·74	24·90	66·27	72·50	66·00	45·63	13·27	64·74
	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00

Adulterants. Besides sugar and starches (which have come to be considered as essential ingredients of certain proprietary cocoa preparations), the usual adulterants are foreign fats (particularly coco-nut oil) to replace the abstracted cocoa butter, farinaceous substances, ground cocoa shells, and pigments such as ferric oxide, ferruginous earth, &c. J. C.

COCOA-NUT OIL GROUP. Under this name the writer comprises a number of vegetable fats which differ from all other vegetable fats by their high saponification values in conjunction with high Reichert-Meissl values. The considerable proportion of volatile fatty acids which the fats belonging to this group contain, brings them into relationship with the milk fats of mammals. They differ, however, from the latter essentially in that they do not contain any butyric acid. The high proportion of volatile fatty acids contained in the members of these groups differentiates them from other fats which are also characterised by high saponification values, but do not contain volatile acids.

The fats belonging to the cocoa-nut oil group are the following: (*a*) Muriti fat, from *Mauritia vinifera* (Mart.); *Acrocomia vinifera* (Oerst.); (*b*) mocaya oil, from *A. sclerocarpa* (Mart.); *Cocos sclerocarpa, C. aculeata* (Jacq.); *Bactris minor* (Gart.); (*c*) cohune oil, from *Attalea cohune* (Mart.); (*d*) maripa fat, from *Palma* (*Attalea*) *maripa* (Aubl.); (*e*) aouara-kernel oil, from *Astrocarpum vulgare* (Mart.); (*f*) palm-nut oil, from the kernels of *Elœis guineensis* (Linn.; Jacq.); (*g*) cocoa-nut oil from *Cocos nucifera* (Linn.) and *Cocus butyracea* (Linn.); (*h*) fat from *Cocos acrocomoides*.

It may be pointed out that aouara-kernel oil and palm-nut oil differ considerably from the corresponding fats contained in the fruit flesh surrounding the seeds (*see* PALM OIL).

All these fats are derived from trees belonging to the palm family. The two most important fats are cocoa-nut oil and palm-kernel oil. The latter will be described subsequently (*v.* PALM KERNEL OIL).

Cocoa-nut oil is the fat obtained from the kernels of the cocoa-nut, especially from those of the two species *Cocos nucifera* (Linn.), and *C. butyracea* (Linn.).

Cocos nucifera grows on all coasts and islands of the tropics; in fact, it may be considered a cosmopolitan of the tropical coast-lines in both hemispheres. The cocoa-nut tree is indigenous to the islands of the Malayan Archipelago, whence the nuts were carried by sea currents towards the east to the Pacific Islands and the coasts of Central America, and towards the west to Ceylon and the east coast of Africa.

Being well protected by the 'coir' (fibres), the seeds are able to germinate on all shores (islands and even coral reefs) where they may be deposited.

The cocoa-nut tree forms large forests, especially on the coast-line of Ceylon, Java, and the Philippines. On account of its manifold uses, the tree has been cultivated early in the history of mankind, and the fruits were, therefore, gathered, as it were, on a commercial scale, not only in the localities named, but also in the South Sea Islands, Madagascar, Mauritius, Ceylon, Zanzibar, the east and west coast of Africa, the Antilles, and the coast-lines of tropical South America.

Cocos butyracea is indigenous to Brazil, and yields, together with *Cocos nucifera* (as also with the other *cocos* species mentioned above), the chief quantities of cocoa-nut fats which are consumed locally. The cocoa-nut oil which is exported to Europe is mainly derived from *Cocos nucifera*.

The cocoa-nut tree flowers when about 6 or 7 years old, and begins to bear fruit from an age of 8 years up to an age of 60 years. The nuts contain a fleshy endosperm, built up from a milky juice, rich in oil. At the period of maturity of the fruit the milky juice has disappeared almost completely, and the endosperm forms the well-known cocoa-nut kernel, inside which the remainder of the milky juice, cocoa-nut milk, is enclosed. The kernel contains from 30 to 40 p.c. of fat, and about 50 p.c. of moisture.

Since the earliest times in the history of mankind, the kernels have been used by the natives of the South Sea Islands, and especially of India, as one of their chief articles of food. The mode of preparing the oil, as practised centuries ago, was of the most primitive kind. The kernels were cut into small pieces and exposed in piles to the sun, when the oil would run off spontaneously. Improved methods consisted in converting the kernels into pulp, placing the latter in vessels perforated with holes, and exposing them to the sun, when the oil would run through the holes. The oil was then collected and carried in bamboo sticks to the market, a practice which up till a few years ago still obtained in the outlying parts of the Philippines. In order to render the process independent of the heat of the sun, as in the rainy season, the kernels were, at a later stage of evolution laid on hurdles, formed from bamboo staves and cocoa-nut leaves, and dried over a slow fire, the fuel for which was derived from the shell of the kernels. In India, where the nuts became at an early date an extensively used food product, the nuts were split into halves by a blow with a sharp instrument, the cocoa-nut milk was poured off, and the halves exposed to the sun to dry, whereby the kernels became readily detachable from the shell. The dried kernels were then triturated and expressed, or the pounded kernels were thrown into boiling water, when the oil rose to the top, and was ready to be skimmed off. The residual mass was used as cattle food ('cocoa-nut poonac'). This process was carried out with special care at Cochin and the coast of Malabar. Hence the reputation of Cochin cocoa-nut oil for best quality has been maintained to this day.

As large proportions of moisture left in the kernel readily lead to putrefaction, a further step in the preservation of the fat was found in drying the kernels thoroughly, so as to remove the bulk of the water. The absence of moisture rendered the growth of fungi impossible, and thus prevented excessive hydrolysis and subsequent rancidity. The process of producing the dried kernel—*copra*—developed into a manufacturing process.

Cocoa-nut oil became first known in Europe in the 18th century, but was not imported in any notable quantities before the year 1820. At present three qualities of oil are distinguished in commerce: (1) *Cochin oil*; (2) *Ceylon oil*; (3) *Copra oil*.

(1) *Cochin oil* represents the finest and whitest quality, and is obtained, as stated above, by boiling the kernels with water and skimming off the oil.

(2) *Ceylon oil* is prepared in a similar manner in the plantations of Ceylon. This oil is not of such high quality as Cochin oil, owing

mainly to the want of care on the part of the natives, as compared with that exercised by the natives of the Malabar coast. Hence Ceylon oil represents, as a rule, a second quality of cocoa-nut oil, and is characterised by a somewhat higher percentage of free fatty acids than is found in Cochin oil. At present, however, in some plantations in Ceylon, managed by Europeans, the same care is exercised as in Cochin, and some brands of Ceylon oil are now imported which yield little in quality to Cochin oil.

(3) *Copra oil* is the oil prepared in modern factories in Europe, United States, Australia, from copra (*i.e.* the dried kernels), which are imported in enormous quantities into these countries. The conversion of the kernel into copra must not only be looked upon as a convenient method for reducing the cost of freight, but, as pointed out above, is pre-eminently a cheap process for preserving the cocoa-nut oil as far as possible.

At present great care is bestowed on the preparation of copra; it is used in growing proportions for the production of edible cocoa-nut oil (*see* EDIBLE OILS), and cocoa-nut stearin (*see* CHOCOLATE FATS). In commerce we differentiate 'sun-dried copra' and 'kiln-dried copra.' The sun-dried copra was considered the better quality, as it gives a white cocoa-nut oil, with only a slight yellow tinge, and could be readily converted into an edible oil. Kiln-dried copra is obtained by a more rapid process, the kernels being dried over a bamboo grating heated by burning underneath it the shells. In these primitive kilns, the fumes obtain ready access to the copra itself, and not only burn it occasionally, but impart to the copra a peculiar empyreumatic smell and a dark colour. Hence copra thus dried yields a yellowish oil which proves refractory in the refining process. At present, however, notable improvements are being introduced in the kiln-drying process, (rotary driers, vacuum driers), so that it may be expected that in the near future kiln-dried copra will take its place next to, or rank equally with, sun-dried copra. Sun-dried copra contains on an average 50 p.c. of fat; in kiln-dried copra the percentage rises to 63 and even 65 p.c. Copra dried by means of hot air contains even as much as 74 p.c.

The copra is treated in oil mills in a similar manner to that in which oleaginous seeds generally are worked up. The meal is expressed twice at a temperature of 55°–60°. The practical yield varies from 63 to 66 p.c., according to the contents of oil in the copra. The expressed oil contains a notable quantity of free fatty acid, the amount depending on the quality of the raw material.

Although the trade in cocoa-nut oil and cocoa-nut products may be said to be still in its infancy, the great importance it has reached may be gathered from the following figures: in the year 1907 the value of the *imports*, *exports*, and home consumption, in the United Kingdom amounted respectively to 857,879*l.*, 424,860*l.*, and 433,019*l.*

In our climate cocoa-nut oil is, at the ordinary temperature, a solid white fat of bland taste, having the peculiar, though not unpleasant, odour of cocoa-nut. The odorous substances in cocoa-nut oil consist chiefly, according to Haller and Lassieur (Compt. rend. 1910, 151, 697), of methylheptylketone and methylnonylketone. These two ketones, together with certain undefined volatile substances, are removed in the process of refining cocoa-nut oil for edible purposes. In order to obtain cocoa-nut stearin (chocolate fat), the liquid glycerides are removed by expression in hydraulic presses, when 50–80 p.c. of the liquid glycerides are expressed. Inferior copra oils also are frequently subjected to the same process, and thus a commercial cocoa-nut stearin is obtained, which, on account of impurities, can only be employed in the manufacture of composite candles and night-lights. The lower qualities of cocoa-nut oil are used in enormous quantities in the manufacture of soap.

Cocoa-nut oil contains large proportions of myristin and, especially, of laurin, small quantities of palmitin, stearin, and *triolein*, and of caprin, caprylin, and caproïn.

The saponification value of cocoa-nut oil lies between 246 and 260; the Reichert-Meissl value of the oil is 7–8; its iodine value about 8–10. Owing to its peculiar chemical composition, cocoa-nut oil is not readily saponified by weak caustic leys. It requires for saponification alkaline leys of high strength, which, however, so easily convert it into soap, that it is only necessary to stir the fat and caustic alkali together at 30°–35°, and allow the mixture to stand. After a short time saponification takes place, with liberation of heat. (Soapmaking by the 'cold process.') Soaps so formed are very hard, and combine with a large amount of water without becoming soft. The soaps are further distinguished by their remarkable property of requiring large quantities of salt to throw them out of their aqueous solution. Hence they are used as 'marine soaps.' J. L.

COCOSITOL *v.* INOSITOL.

CODEÏNE *v.* VEGETO-ALKALOIDS.

COD LIVER OIL is obtained from the liver of the cod, *Gadus morrhua* (and of the dorsch, the young of *G. morrhua*, formerly considered a separate species, *G. callarius*). The cod appears annually at certain times in enormous shoals on the coasts of the northern seas, chiefly on the coasts of Norway, Scotland, Newfoundland, the east of the United States and of Canada, the west coast of the United States and the coasts of Japan and Siberia. The best-known and oldest fishing-grounds are those of Norway, where the fish make their appearance at regular intervals of the year.

In the early years of the manufacture of cod liver oil, the livers were heaped up in barrels and allowed to undergo a process of spontaneous putrefaction, whereby the liver cells burst and the oil exuded. The oil so obtained was contaminated with decomposition products of the liver, and possessed that rank odour and nauseous taste with which even nowadays popular prejudice associates medicinal cod liver oil. Of late years the manufacture of cod liver oil has been carried out in a scientific manner, and the best oil is at present obtained by steaming the livers in the freshest state obtainable. The livers are washed immediately they are taken out of the body of the fish, and placed in jacketed vessels in which they are heated to a

temperature of 70°-80°, when the cells burst and the oil flows off. This oil is known as 'raw medicinal oil,' and is consumed as 'congealing oil' in those countries where the Pharmacopœia permits congealing oils. The British Pharmacopœia prescribes, however, a non-congealing oil, which will not "set" at the freezing-point. It is prepared by cooling the crude medicinal oil below zero and filtering it at a temperature of −10°. The 'stearine' is sold as fish stearin of best quality for soap-making purposes. All unsound livers, and those which have been exposed for some time to the atmosphere, are then worked up for 'brown oil.' This oil is, of course, a genuine cod liver oil, but is (or should be considered) unfit for consumption, and is mostly used up in leather industries, under the name 'brown cod oil' or 'cod oil.'

The pure medicinal oil is pale yellow or light yellow, and the best qualities have a slight fishy odour only, and a by no means unpleasant taste. Such oil has a sp.gr. of about 0·922–0·93 at 15°, and a saponification value of 175–190, and an iodine value of 140–175. The best qualities have an iodine value of about 175, for the longer the livers have been exposed, the lower will be the iodine value, so that this value alone may indicate, preliminarily, a good medicinal oil. The chemical composition of the cod liver oil glycerides is not yet completely known. Small quantities of palmitin occur in the oil, and are the cause of the separation of 'stearine.' The older statement that small quantities of lower saturated fatty acids, such as those of acetic, butyric, valeric, and capric acids occur in cod liver oil must be rejected, these statements being due to the fact that the cod liver oil in which those volatile fatty acids were found had already undergone decomposition. The greater number of the liquid fatty acids in cod liver oil are not identified. Among the unsaturated fatty acids there occurs undoubtedly *clupanodonic acid;* this can be identified and isolated by means of its octobromide, which does not melt at 200°, and decomposes, with blackening above that temperature.

The therapeutic value of cod liver oil which was attributed to the organic bases occurring in badly rendered cod liver oil must (in the author's opinion) be ascribed rather to the easy manner in which cod liver oil is digested than to any specific constituent, for the purest cod liver oil practically represents a mixture of pure glycerides with a small amount only of cholesterol and other unsaponifiable substances.

Like all liver oils, cod liver oil may be identified by the colour test which it gives with concentrated sulphuric acid in a solution of carbon tetrachloride or carbon disulphide. The better a cod liver oil is in quality, the fainter is the sulphuric acid colour test; this points to the fact that the colour test is due to small quantities of foreign substances which are dissolved by the oil from the tissues of the liver. J. L.

CŒLESTIN *v.* STRONTIUM.

ÇŒLINE, CŒRULEAN BLUE, CŒRULEUM *v.* COBALT; also PIGMENTS.

CŒRULEÏN, *Anthracene green* (*v.* ALIZARIN AND ALLIED COLOURING MATTERS).

CŒRULIGNOL $C_3H_7{\cdot}C_6H_3{\cdot}(OH)OCH_3$. A colourless oil of a burning aromatic taste, and a smell resembling creosote, obtained from beech pine and fir tars. Boils at 240°-241°; sp.gr. 1·0564 at 15°. It is somewhat soluble in water, freely soluble in alcohol, ether, and acetic acid. It is coloured red by sulphuric acid, and dark-brown by potassium hydroxide in contact with the air. In alcoholic solution it gives with barium hydroxide a characteristic deep-blue colouration. Ferric chloride in alcoholic solution gives a green, in aqueous solution a deep-red, colouration. Cœrulignol is decomposed on treating with hydrochloric acid at 145°, according to the equation

$$C_{10}H_{14}O_2 + HCl = C_9H_{12}O_2 + CH_3Cl.$$

CŒRULIGNONE (*Cedriret*)

$$(CH_3O)_2C_6H_2{\cdot}O{\cdot}O{\cdot}C_6H_2(CH_3O)_2.$$

A steel-blue crystalline solid obtained by oxidising pyrogalloldimethylether in acetic acid solution with potassium dichromate (Hofmann, Ber. 11, 335). It combines with primary amines to give deep-blue dyestuffs (Liebermann and Flatau, *ibid.* 1897, 234; Moir, Chem. Soc. Proc. 1906, 110; 1907, 307) (*v.* CEDRIRET).

COFFEE. The beverage known as 'coffee' is prepared from the seeds (dried, roasted, and ground) of *Coffea arabica* (Linn.), an evergreen shrub, indigenous to North-East Africa, and Arabia. The use of coffee has been known from time immemorial in Abyssinia, whence it spread to the neighbouring Mahometan countries (where its use was at various times forbidden as being an 'intoxicating' beverage), and subsequently to all parts of the civilised world. It did not find its way into Europe, however, until the beginning of the 17th century. It was introduced into England in 1652, and rapidly spread in popular favour in spite of heavy taxation and attempts to suppress the 'coffee houses,' for political reasons, until its importation reached a maximum of 37½ million lbs. in 1847. Since then the consumption has declined, due, no doubt, chiefly to the greatly extended use of tea, and partly to the introduction of coffee substitutes. At the present time (1911), the consumption of coffee in the United Kingdom is less than 30 million lbs., or less than ¾ lb. per head. In the principal coffee-drinking countries of the world the consumption of coffee per head of the population is as follows: Holland, from 14 to 15 lbs.; United States of America, 12 lbs.; Scandinavia, nearly 12 lbs.; Germany, 7 lbs.; and France, 4 lbs.

The coffee tree belongs to the natural order *Cinchonaceæ*, which embraces, according to Lindley and Paxton, two species, *C. arabica* and *C. paniculata* (Aubl.). Other botanists distinguish many other species, as *C. microcarpa, C. umbellata, C. acuminata, C. subsessilis, C. laurina, C. racemosa, C. bengalensis, C. indica,* &c. Some of these are probably only varieties. However this may be, four species distinct from each other are now grown: (1) Arabian or Mocha coffee, having short upright branches with a brittle leaf, and seeds usually single in the berries. (2) Jamaica coffee, bearing longer and more pliable branches, a tougher leaf, and seeds almost always double in the berries. (3) East India or Bengal coffee, of which the leaf is smaller than the Jamaica variety, and the berry very small. (4) Liberian coffee (*C. liberica*) is taller and has larger leaves and fruit than the preceding varieties, but owing to its coarse

flavour, it was not until recently of much commercial use. It has, however, rapidly attained importance on account of its hardy habit and power of resistance to disease, and is now largely cultivated by grafting on to its stem the more delicate and highly esteemed Arabian coffee. Trees growing wild in the Cingalese jungle attain a height of 14–18 feet; but under cultivation and subjected to systematic pruning, the plant rarely exceeds 6–9 feet. Within the tropics the coffee tree succeeds best at 1200–3000 feet above the sea-level, but grows at a height of 6000 feet. When the mean temperature is about 70°, it may be grown as far as lat. 36°. It is cultivated in the West Indies, Mexico, Central America, Brazil, and Cayenne; in Western Africa, Egypt, Mozambique, and Natal; in Arabia, India, Ceylon, Siam, Sumatra, Java, Celebes, and other parts of the Eastern Archipelago, Fiji, and the islands of the Pacific. At the present time more than three-quarters of the world's supply comes from Brazil.

The coffee consumed in the United Kingdom comes principally from Costa Rica and British India as regards the finer qualities, and the inferior grades from Brazil.

The manner of forming plantations varies somewhat in different countries. The surface soil should be good and the subsoil not too stiff. Perhaps the best soil is that known in Brazil as 'terra roxa,' a topsoil of red clay 3 or 4 feet thick, with a subsoil of gravel. Virgin forest land is as a rule, found very suitable. Shelter from wind is most important, and a wet soil is fatal. Steep slopes are unsuitable owing to rain wash. The loss due to this cause should be repaired by good manure, well-rotted dung and ground bones being the best. The young plants may be reared in nurseries, whence they are transplanted to their permanent position, or they may be gathered out of the old plantations; the age at which this is done varies, as in Brazil where the shrub is usually two years old on its removal, or as in the West Indies where it is planted out at 6 months. Fruit is produced in the fourth year, and continues to be gathered for several years.

The tree blossoms and bears fruit practically all the year round, and the fruit takes about 4 months to ripen. There is thus in some places an almost perpetual crop, but, as a rule, there are two principal harvest seasons in the year.

The coffee fruit consists of a bilobed berry somewhat resembling a small elongated cherry (by which term it is described commercially). The fleshy pericarp changes colour, as the fruit ripens, from green through yellow and red to a deep crimson. When dried, it blackens and becomes hard and brittle, resembling a shell or husk. Beneath the skin of the pericarp is a saccharine and somewhat glutinous pulp containing the seeds, which are usually double, lying face to face, but sometimes occurring singly. Each seed or 'bean' is enclosed in two membranous coverings—an outer, consisting of tough buff-coloured tissue, technically known as 'parchment,' which becomes loose and readily separates on drying; and an inner film of thin white tissue, closely adherent to the bean, and known as the 'silver skin.'

The principal methods in vogue for gathering and preparing the coffee berries for commerce are as follows. In Arabia, Egypt, and the Antilles, the berry is left on the tree till completely dried, when it is easily shaken down and the dry outer envelope and the parchment removed by pounding in a mortar, beating with a flail, or simply rubbing in the hands. In many other places the berries are gathered by hand as soon as ripe but not dry, and are spread out on the ground in layers from 4 to 6 inches deep. These are exposed to the sun's heat for 3 or 4 weeks, with frequent turning by means of spades, when the bean becomes easily removable from the fruit by gentle trituration. As this process of drying sometimes imparts to the coffee a disagreeable flavour owing to putrefactive changes in the pulp, recourse is frequently had to artificial heat. The most modern method is to 'pulp' the berries by crushing between rollers so as not to injure the beans, which are then subjected to a fermenting process in tanks, with or without the addition of water, after which they are separated from the pulp by 'washing,' and dried, either by the sun or by artificial means. Coffee beans in the form of 'cherry' rarely enter into commerce, but frequently retain the parchment and silver skin, which, however, before roasting, are removed by rollers and separated by winnowing. They are then graded into different sizes by special machinery, which also separates the round or 'pea-berries' from the ordinary flat-faced beans. The colour of coffee beans varies from a pale-yellow passing through various shades of green to a slatey grey. The following table will indicate the variations in size:—

	No. of seeds in a measure holding 50 grams of water.
Fine brown Java	187
Fine Mysore	198
Fine Neilgherry	203
Costa Rica	203
Good ordinary Guatemala	207
Good La Guayra	210
Good average Santos	213
Fine long-berry Mocha	217
Good ordinary Java	223
Fine Ceylon plantation	225
Good average Rio	236
Medium plantation (Ceylon)	238
Manilla	248
Ordinary Mocha	270
West African	313

Coffee undergoes important changes in the process of roasting, the object of which process is to develop its aroma and to destroy its toughness so that it may easily be reduced to powder. Great care is necessary to ensure an equable roasting of all the beans, and to attain the exact point at which torrefaction should cease. If, on the one hand, rawness is not removed, the flavour of the bean is not developed, and the coffee is hard to grind; on the other hand, if too much heat is permitted, carbonisation takes place, and a strong empyreumatic flavour is produced, which renders the coffee infusion nauseous.

The roasting process is conducted in cylinders (preferably of strong wire gauze to permit of the escape of steam and other volatile products as fast as they are formed) heated by coke fires or gas. The loss in weight is from 15 to 18 p.c., of which about one-half is due to moisture,

and the rest chiefly to volatile products derived from the fat, and from the sugar during the conversion of the latter into caramel. There is also some loss of caffeine. At the same time, an empyreumatic oily substance is developed, known as *caffeol*, which, in spite of its small amount, imparts to roasted coffee much of its characteristic aroma. The most favourable temperature for developing the maximum aroma during roasting is a little above 200°. After roasting, it is most important that the beans should be rapidly cooled, and this is effected by spreading them on a large sieve through the meshes of which they cannot pass, but through which the air is forcibly drawn by means of a powerful exhaust connected with a closed chamber immediately below the sieve. Since the essential oil rapidly escapes after the bean is broken up, coffee should not be ground until required for infusion.

O. Bernheimer (Wien. Akad. 81, [2] 1032, 1042) found that during the roasting of coffee, water vapour is first given off, then suddenly an evolution of carbonic anhydride, and distillation of volatile substances commences. The distillate consists of an aqueous liquid and a solid part. The former contains caffeine, caffeol, acetic acid, quinol, methylamine, and acetone; the latter consists of fatty acids, chiefly palmitic. Pyrrol escapes during roasting. Of fatty acids, 0·48 p.c. of the coffee employed was volatilised; of caffeine, 0·18 p.c.; and of caffeol, 0·05 p.c.

Bernheimer found that raw coffee beans (50 kg.) roasted in a revolving drum yielded a liquid distillate (5 litres) and a solid portion (680 grams) floating thereon. The uncondensable vapours contained carbonic anhydride, and, on passing them through dilute hydrochloric acid, a resinous body was deposited, having the appearance of pyrrol-red.

A. *Liquid distillate.*—The crude liquid distillate filtered from solid particles has a yellow colour and the fragrant odour of coffee. On agitating it with ether, and evaporating the ethereal extract over the water-bath, a dark heavy oil was obtained, smelling like coffee, and yielding, on redistillation, first a few drops of liquid having the odour of acetone, afterwards, for the most part, acetic acid and water. The thermometer then rose quickly to 200°, above which point there passed over an oil smelling like coffee, the temperature at the same time rising to 300°. Above this point there passed over a very small quantity of liquid, which immediately solidified to a mass having the buttery aspect and rancid odour of the higher fatty acids. This portion, and the liquid which passed over from 200° to 300°, were neutralised with sodium carbonate, whereupon a thick dark-coloured oil was thrown down, which was separated from the supernatant liquid by means of a tap-funnel, and washed with water rendered very slightly alkaline by potash.

The alkaline wash waters contained no fatty acids, but, when acidified with sulphuric acid and agitated with ether, they yielded a substance which, after evaporation of the ether, filled the liquid with a pulp of crystals, and after precipitation crystallised in colourless needles, exhibiting the characters of *quinol* (m.p. 171°), converted into quinhydrone by the action of ferric chloride.

The oil above mentioned, designated by Bernheimer as *caffeol*, was dried over calcium chloride and fractionally distilled, the greater part passing over from 195° to 197°. The distillate smells very strongly of coffee, is apparently insoluble in cold water, but imparts to it the characteristic odour; slightly soluble in hot water, very slightly in aqueous potash, very easily in alcohol and ether, the alcoholic solution giving, with ferric chloride, a red colouration, which does not disappear on addition of sodium carbonate. Analysis led to the formula $C_8H_{10}O_2$. Caffeol is oxidised by chromic acid mixture, without formation of any definite products. By fusion with potash it yields salicylic acid. The portion of the crude liquid distillate not taken up by ether, when concentrated over the water-bath, yielded groups of needle-shaped crystals, exhibiting the composition and properties of *caffeine* $C_8H_{10}N_4O_2$ (0·28 p.c. of the coffee). The mother liquor was found to contain *methylamine* and *trimethylamine*.

B. *Solid distillate.*—The black mass floating on the crude liquid distillate was found, by a preliminary examination, to consist of a mixture of the higher fatty acids. By saponification, and treatment of the product by Heintz's method of separation, this mixture yielded, as chief constituent, *palmitic acid* melting at 60°, and a very small quantity of another acid having a melting-point a few degrees higher than that of lauric acid.

The chemical composition of coffee has been investigated by many chemists with various results. The following table gives analyses by O. Levesic (Arch. Pharm. [3] 8, 294) of some of the principal commercial varieties of coffee:—

—	Gummy matter	Caffeine	Fat	Tannic and caffetannic acids	Cellulose	Ash	Potash	Phosphoric acid
Finest Jamaica plantation	25·3	1·43	14·76	22·7	33·8	3·8	1·87	0·33
Finest green Mocha	22·6	0·64	21·79	23·1	29·9	4·1	2·13	0·42
Ceylon plantation	23·8	1·53	14·87	20·9	36·0	4·0	—	0·27
Washed Rio	27·4	1·14	15·95	20·9	32·5	4·5	—	0·51
Costa Rica	20·6	1·18	21·12	21·1	33·0	4·9	—	0·46
Malabar	25·8	0·88	18·80	20·7	31·9	4·3	—	0·60
East Indian	24·4	1·01	17·00	19·5	36·4	—	—	—

Commaille (Mon. Sci. [3] 6, 779) found in undressed Mysore coffee:

Hygroscopic water (extremes of 24 determinations)	6·3 to 15·7
Fatty matters	12·68
Glucose	2·60
Dextrin	—
Legumin-casein	1·52
Albumen	1·04
Total quantity of caffeine	0·42 to 1·31
Ash	3·882
Coffee extract with cold water	24·97
,, ,, ,, warm water	37·20
Coffee extract with alcohol of 60 p.c.	23·15

Dragendorff gives the following results of analyses of 25 different samples of coffee from Ceylon, Java, Malabar, Mocha, Mysore, and other places :—

	Maximum per cent.	Minimum per cent.	Mean per cent.
Caffeine	2·21	0·64	1·16
Ash	4·87	3·83	4·41
Phosphoric acid	0·72	0·28	0·42

The principal constituents of coffee are alkaloids (caffeine and caffearine), caffetannic acid, cellulose, fat, gum, protein, sugar, water, and mineral matter.

Caffeine $C_5H(CH_3)_3N_4O_2$, trimethylxanthine, is identical both chemically and physiologically with theine, the alkaloid of tea, and is closely related to theobromine (dimethylxanthine), the principal alkaloid of cocoa (*q.v.*). According to Payen (Ann. Chim. Phys. [3] 16, 108), caffeine is present as a caffetannate. Gorter (Annalen, 1908, 358, 327) states that caffeine occurs in coffee combined with potassium as potassium caffeinechlorogenate $C_{32}H_{36}O_{12}K_2(C_8H_{10}N_4O_2)_2$, $2H_2O$. When pure it consists of white silky needles, slightly bitter and odourless, almost insoluble in ether, sparingly soluble in cold water and alcohol, but more soluble in hot water, and readily soluble in chloroform, by means of which it may be extracted from coffee. The crystals begin to sublime below the boiling-point of water.

Caffeine is found also in guarana leaves, kola-nut, maté or Paraguay tea and to a small extent in cocoa as well as in coffee and tea, and gives to these their exhilarating qualities. Taken in excess, caffeine is a poison. In coffee it is present to the extent of from 0·6 to 2·2 p.c., the average being 1·1 p.c. Lendrich and Nottbohm (Zeitsch. Nahr. Genussm. 1909, 18, 299) report nearly 3 p.c. of caffeine in certain African coffees, whilst in Madagascar and other islands off the east coast of Africa a variety of coffee has been found entirely devoid of caffeine. A coffee has recently been placed on the market after being deprived of practically the whole of its caffeine.

Numerous methods have been proposed for the estimation of caffeine. That of Lendrich and Nottbohm is detailed in the Analyst, 1909, 214. A good method, sufficiently accurate for ordinary purposes, is that given in Jour. Anal. Chem. 4, 4, 390.

Another alkaloid, *Caffearine*, having narcotic properties, is stated by Paladino (Gazz. chim. ital. xxv. 1895) to be present in coffee in very small quantity.

Caffetannic acid presents certain of the characteristics of tannin (which, however, is not found in roasted coffee) and to it the bitter taste of coffee is chiefly due. It is very susceptible to change, and its composition has been much disputed. According to Gorter (*vide supra*), it is a mixture of a new acid discovered by him and called *caffalic acid*, with chlorogenic acid. A method for its estimation in coffee has been devised by Krug (U.S.A. Dept. of Agric. Div. of Chem. Bull. 13, 908). According to Bell, caffetannic acid is present in coffee to the extent of from 3 to 5 p.c., and when distilled with manganese dioxide and sulphuric acid yields quinone.

Cellulose.—In coffee this is of a very hard and horny character, and difficult to define under the microscope, especially after roasting, although the chief characteristics of the cellular tissue are more or less retained. Coffee cellulose is dissolved by an ammoniacal solution of copper oxide, and gives a blue colour with sulphuric acid and iodine. Remnants of the silver skin are always present even after roasting, and its structure, a thin membrane with adherent, thick-walled, spindle-shaped, and hollow cells, is quite peculiar to coffee.

Fat forms a considerable constituent of coffee, varying from 10 to over 20 p.c. A loss occurs in roasting, due to the separation of volatile fatty acids. When pure, coffee fat is white, inodorous, and of the consistency of butter, melting at 37·5°.

Protein, chiefly in the form of insoluble albuminoids, occurs in coffee to the extent of from 10 to 14 p.c., the soluble albuminoids constituting about 2 p.c. There is but little difference in this respect between raw and roasted coffee.

Sugar.—König and Bell found from 5 to 9 p.c. of sugar in raw coffee, but this practically disappears in roasting, being almost entirely converted into caramel. Herfeldt and Stutzer (Zeitsch. angew. Chem. 1895, 469) state that sugar is not present as such in the raw bean, but only in the form of a glucoside. Bell, however, found that when the saccharine extract of the beans is boiled with a little dilute sulphuric acid, a quantity of glucose is obtained nearly equivalent to the weight of dry extract operated upon, a result inconsistent with the existence of sugar as a glucoside. Bell considers that this sugar is not present as sucrose, since it is not inverted even after prolonged boiling with acetic acid. On the other hand, the chemists of the United States Department of Agriculture have isolated cane sugar in considerable amount as pure, well-defined crystals (*v.* Bulletin, 13). It is usually accompanied by some invert sugar probably formed during the process of extraction, and a small percentage of dextrin. Starch is absent in the coffee bean.

Water.—The moisture in raw coffee varies from 8 to 14 p.c., the average being about 11 p.c. After roasting, it rarely exceeds 3 p.c., and frequently falls as low as 0·5 p.c.

Mineral matter.—The total amount of ash varies from 3·5 to 4·0 p.c. in raw, and from 4·0 to 5·0 p.c. in roasted coffee. The composition of the ash is shown in the following table (U.S.A. Dept. of Agric. Div. of Chem. Bull. 13, 904) :—

Constituents	Mocha	Maracaibo	Java	Rio
Sand	1·44	0·72	0·74	1·34
Silica (SiO_2)	0·88	0·88	0·91	0·69
Ferric oxide (Fe_2O_3)	0·89	0·89	1·16	1·77
Lime (CaO)	7·18	5·06	4·84	4·94
Magnesia (MgO)	10·68	11·30	11·35	10·60
Potash (K_2O)	59·84	61·82	62·08	63·60
Soda (Na_2O)	0·48	0·44	—	0·17
Phosphoric acid (P_2O_5)	12·93	13·20	14·09	11·53
Sulphuric acid (SO_3)	4·43	5·10	4·10	4·88
Chlorine (Cl)	1·25	0·59	0·73	0·48
	100·00	100·00	100·00	100·00

The principal constituents are potash, magnesia, lime, and phosphoric acid. Ludwig, in his analyses of various parts of the Brazilian coffee tree, shows that the silica increases from the root upwards to the leaves and pericarp of the fruit, after which it declines in the parchment skin, and is nearly absent in the bean (Arch. Pharm. [3] 1, 482). Graham, Stenhouse, and Campbell inferred that sodium compounds are entirely absent in coffee (*vide* table in Bell's Food Adulteration, 46), but although this is not absolutely correct, the amount, as shown in the above table, is very minute.

Adulteration of coffee is very common, and the number and variety of the adulterants is almost unlimited.

Colouring is frequently employed in order to disguise damaged beans and give them the appearance of superior quality, a practice analogous to the 'facing' of tea. The substances most commonly employed are, for the raw beans, chrome yellow, yellow ochre, indigo, Prussian blue, azo- dyes, and soapstone for polishing; and for the roasted beans, burnt amber, oxide of iron, Venetian red, ferruginous earth and clay. The inorganic colouring matters are best sought for in the ash or in the sediment obtained by shaking the beans in cold water; indigo and Prussian blue by their usual reactions; and other organic colouring matters after extracting them with alcohol.

Glazing is a process resorted to for the alleged purpose of improving the keeping properties of the roasted beans, and the substances used, a mixture of egg albumen with glucose or gum, are said to have the effect of clarifying the infusion. The improved appearance of the beans and increased weight due to the retention of moisture, are probably also important considerations. The latter result is sometimes attained by the addition of sugar before roasting, or by actually steaming the beans and coating them with glycerine, palm oil, or vaseline, to prevent evaporation of moisture. Bertarelli (Zeitsch. Nahr. Genussm. 1900, iii. 681) describes the adulteration of roasted coffee beans with a solution of borax, which not only gives the beans a glossy appearance, but also adds as much as 12 p.c. to their weight.

Coffee substitutes comprise a large number of vegetable substances, roasted and ground, and having for their object either the production of a stronger infusion than can be obtained from coffee alone, or the simulation of coffee in order to give weight by the use of thick-walled vegetable tissue of hard or leathery consistency. The former, of which chicory is the type, includes acorns, beet refuse, biscuits, bran, cereals (barley, buckwheat, maize, malt, oats, rye, and wheat); caramel (burnt sugar); carrots, dandelion root, figs, lupin seeds, mangolds, parsnips, peas, beans, and other leguminous seeds, turnip, &c.; whilst the latter comprise such substances as coffee husks, cassia seeds, date stones, grape stones, locust or carob beans, sawdust, vegetable ivory dust, &c.

Imitation coffee.—Although adulteration is naturally more prevalent in ground coffee than in the beans, yet the latter are frequently prepared artificially and on a large scale from the above adulterants (generally without any admixture of coffee), held together by means of gum, molasses, or stiff clay, and skilfully moulded into the form of coffee beans.

The detection of the adulterants above referred to is best effected by means of the microscope. By simply digesting with water, a ready means is afforded of differentiating between the pale soft-walled tissues of cereals and roots and the dark-coloured and hard-walled tissue of coffee. The former may readily be detected and identified by the presence and characteristics of their starch, coffee (and chicory) being practically free from starch. The use of bleaching reagents is of great assistance in the microscopical examination, and reference might usefully be made to the drawings and photographs reproduced in the works of Bell, Leach, Villiers et Collin, and Wiley, and in the Coffee Report of Graham, Stenhouse, and Campbell, referred to below.

The chemical differences between coffee and its adulterants are also strongly marked, as mixtures usually give high aqueous extract and sugar, and low fat and caffeine. The density is a useful factor in detecting the sophistication of coffee, and, in particular, the artificial moistening of the berries. In the Paris Municipal Laboratory, Regnault's volumenometer, as modified by Dupré, is used for this purpose. According to the French chemists, the density of raw coffee varies between 1·041 and 1·368, and that of roasted coffee between 0·500 and 0·635.

By far the most important adulterant of coffee is *chicory* (*q.v.*), but owing to the public preference for an admixture of chicory with coffee, it is now regarded in the light of an adjunct to rather than an adulterant of coffee,

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provided its presence in the mixture is disclosed. Chicory has little in common with coffee except a considerable proportion of sugar, which is converted into caramel in the roasting, and thus imparts to the infusion a bitter taste and aroma somewhat resembling that of coffee. This and the stronger infusion obtained as well as the comparative cheapness of chicory and similar substances, has, no doubt, led to the present extensive use of chicory and other coffee substitutes.

An elaborate research into the nature of coffee and chicory, with a view to the detection of adulteration, was made at the instance of the Commissioners of Inland Revenue in 1852 by some of the leading botanists and chemists of the day, viz. Lindley and Hooker, and Graham, Stenhouse, and Campbell, and the results, chemical and physical, as well as microscopical, embodied in their reports are of great practical value even at the present time.

The following table by Graham, Stenhouse, and Campbell, shows the sp.gr. at 60°F. of solutions made by treating one part of each of the substances named (roasted and finely ground) with 10 parts of water (by weight), raising the mixture to boiling-point, where it is maintained for half a minute, then filtering and cooling :—

SPECIFIC GRAVITIES OF SOLUTIONS AT 60° F.
One Part of Substance to 10 *Parts of Water.*

Spent tan	1002·1
Date stones	1002·9
Lupin seed	1005·7
Acorns	1007·3
Peas	1007·3
Mocha coffee	1008·0
Deans	1008·4
Neilgherry coffee	1008·4
Plantation Ceylon coffee	1008·7
Java coffee	1008·7
Jamaica coffee	1008·7
Native Ceylon coffee	1009·0
Costa Rica coffee	1009·5
Parsnips	1014·3
Carrots	1017·1
Black malt	1021·2
Turnips	1021·4
Rye malt	1021·6
English chicory	1021·7
Dandelion root	1021·9
Red beet	1022·1
Foreign chicory	1022·6
Guernsey chicory	1023·2
Mangold wurzel	1023 5
Roasted figs	1024·9
Maize	1025·3
Bread raspings	1026·3

It will be seen from the above table that the low sp.gr. of the coffee infusion distinguishes it from the roots and cereals, and when chicory is the only substance admixed with the coffee, its percentage may be calculated with approximate accuracy by a comparison of the density of the infusion of the mixture with the average densities of coffee and chicory given in the above table.

The same observers lay stress on the relative colouring power of roasted coffee and chicory, the latter being four and a half times as great as the former. This property affords a simple device for detecting the presence of roasted chicory or other substances containing caramel when admixed with coffee. A few grains of the sample are placed on the surface of cold water in a glass, without stirring, when, if roasted chicory or similar substance be present, each particle emits a yellowish-brown coloured cloud, which is rapidly diffused in streaks through the water till the whole acquires a brownish colour, whilst pure coffee gives practically no colour to the water in similar circumstances. The chicory readily sinks, whilst nearly the whole of the coffee floats.

If examined under the microscope, the sediment of chicory which reaches the bottom of the vessel will be found to exhibit the characteristic loose, large cells, with dotted vessels and branching lactiferous ducts. Even to the touch the difference is evident, for, whilst chicory under these conditions will feel soft and smooth, the coffee grains remain hard and gritty.

A. Winter Blyth (Foods; their Composition and Analysis, 359) gives the following summary of the influence of chicory on the coffee mixture :—

(1) It decreases the gum, the latter seldom rising in chicory to more than 15 p.c., whilst in coffee it has not been found less than from 21 to 28 p.c.

(2) It increases the sugar, roasted coffee having seldom so much as 2 p.c. of sugar; whilst chicory, when roasted, has at least 8 or 9 p.c.

(3) It decreases the fatty matter, the fat of chicory ranging from 1 to over 2 p.c., that of coffee being about 14 to over 20 p.c.

(4) It decreases the tannic and caffeotannic acids, chicory being destitute of tannin.

(5) It decreases the caffeine, chicory possessing no alkaloid.

(6) It profoundly modifies the constitution of the ash, especially by introducing silica, which is not found to any great extent in coffee ash.

Graham, Stenhouse, and Campbell laid stress upon the presence of silica as a means of detection of the admixture of chicory. Their analysis, showing the principal differences in the composition of the respective ashes, gives :

	In coffee ash	In chicory ash
Silica and sand	——	10·69 to 35·85
Carbonic acid	14·92	1·78 „ 3·19
Ferric oxide	0·44 to 0·98	3·13 „ 5·32
Chlorine	0·26 „ 1·11	3·28 „ 4·93

There is a marked difference in the proportion of ash soluble in water, that from coffee amounting to from 75 to 85 p.c., and in chicory from 21 to 35 p.c.

Negro or *Mogdad coffee* consists of the seeds of *Cassia occidentalis*. It contains no caffeine nor starch, and its infusion more nearly approaches the character of genuine coffee than any other known coffee substitute.

Mussaendar coffee is derived from the seeds of *Guertnera vaginata*. It contains no caffeine.

French coffee is a description commonly applied to a mixture of coffee with burnt sugar and a large proportion of chicory. As the latter ingredients readily absorb moisture on exposure to the air, such mixtures are usually preserved in tins.

Various fraudulent coffee substitutes have

been imposed upon the public by specious advertising under fancy names, and as possessing certain desirable qualities not found in coffee. Such are *Kunst kaffee*, consisting of roasted roots or cereals, and often moulded into the form of coffee beans; *Pelotas coffee* and *Coffee surrogate*, made from ground acorns; *Date coffee* from date stones, or torrified dates mixed with a small proportion of coffee; and many others.

The grosser forms of adulteration above referred to are much more prevalent in the coffee-drinking countries of the continent of Europe and in the United States of America than in the United Kingdom. J. C.

COGNAC *v.* BRANDY.

COKE MANUFACTURE AND THE RECOVERY OF BY-PRODUCTS.

Introduction.—Previous to the early nineties, practically the whole of British coke was made in the old beehive oven, which, as will be seen in the following, is a semi-combustion process, involving the loss of the whole gas and by-products, together with a portion of the possible coke yield. With the gradual disappearance of the old prejudices against coke made in by-product ovens, the latter and much more highly economical process began to assert itself, and in 1898, 1·25 million tons of coal were being carbonised in by-product coke ovens; in 1905 the quantity of coal so treated reached 3·31 millions; and in 1909, 7·5 millions. With this rapid adoption of the by-product coking process, it is necessary to confine the following article to a description of modern coking methods viewed from a by-product standpoint, with only a passing reference to the wasteful beehive process.

History of the by-product coking process.—The earliest reference which we can find of any observation being made on coal as a source of by-products is that contained in the memoirs of Johann Joachim Becher, dating about the end of the 17th century; Becher states that he has found means for treating coal 'so that it no longer smoakes nor stinks,' and in doing so made a tar equal to the Swedish.

The use of coke in iron smelting became general within 50 years of Becher's discovery, and a French metallurgist, De Gensanne, describes a process working at Sulzbach near Saarbrucken prior to 1768, where coal was coked for iron smelting, tar being recovered as a by-product; Stahl is said to have been the inventor of this process, and he produced therefrom an 'oil,' bitumen, sal-ammoniac, and lampblack.

In 1781 Archibald, Earl of Dundonald, was granted a patent for 'allowing coals to burn or ignite without flaming, so by their own heat to throw off the tar or oils that they contain.' Dundonald stated that the only method whereby tars could be obtained prior to his discovery, was by a distillation in closed retorts, where the admission of external air was prevented, and where other coals were required for heating besides the coals contained in the closed vessel. It is interesting to note that Dundonald was perfectly aware of distillation in closed retorts, which is the basis of modern by-product coking methods, and it is also evident that Dundonald's knowledge of closed retorts was 16 years previous to the introduction of coal gas for street and household illumination in 1797.

In 1838 Frederick Neville obtained protection for an invention which consisted in heating ordinary gas retorts by the waste heat from beehive coke ovens, the distilled gases from the retorts being passed through condensing and scrubbing applicances. William Newton, in 1852, introduced the use of an aspirator or pump for withdrawing the gases from coke ovens through condensers and scrubbers. Newton likewise mentions the use of acids for removing the ammonia from the gases. In 1860 W. H. Kingston patented a coke oven provided with external furnace, from which the heat evolved by the combustion of an auxiliary supply of coal was conducted round the oven through a system of flues; the evolved gases were passed through a series of pipes and condensing vessels for the recovery of the by-products. Kingston's patent is especially noteworthy, since he recognises that the true method for the recovery of by-products from coal lies in heating the coal in closed chambers, and not in chambers to which air is admitted.

In 1856 Knab erected a coal-distillation plant at Commentry, on the closed-retort system with bottom flues, but made no attempt to recover by-products. Later Knab was joined by Carvès, who introduced an improved method of heating by side flues in addition to the bottom flues, thus obtaining a more even distribution of temperature and a quicker rate of carbonisation. Carvès likewise first utilised the gases from which the by-products had been extracted in the side-wall flues, in addition to the auxiliary coal as employed by Knab. The Knab-Carvès ovens at Commentry gave the following results:—

Large coke	70·00
Breeze	1·50
Dust	2·50
Graphite	0·50
Tar	4·00
Ammoniacal liquor	9·00
Gas	10·58
Loss	1·92
	100·00

Further plants on the Carvès system were erected at Bessèges and Terre-Moire, near St. Etienne, between the years 1866 and 1873, and were still further improved; the Carvès ovens working at Bessèges in 1880 were built with carbonising chambers only 24 inches wide, to facilitate rapid heat penetration and quick carbonisation. In 1881 Mr. H. Simon of Manchester introduced a recuperator, whereby the air necessary for the combustion of the gas in the side-wall flues of the Carvès oven was preheated by the waste gases escaping from the flues, and thus the rate of carbonisation was still further increased, the combined work of the two investigators resulting in the well-known Simon-Carvès oven, which may be held to be the precursor of the modern by-product coking retort.

Following on the success of the Simon-Carvès process, other coke-oven patents were filed, viz Semet-Solvay, 1880; Hüssener, 1881; Lürmann, 1882; and Brunck, 1883; but although development was rapid on the Continent, little was done in this country before the nineties, owing to the prejudice of iron smelters against by-product coke; that this

prejudice has now disappeared will be seen from the rapid adoption of the process, indicated by the figures at the beginning of these notes. The by-product coking plants which have generally found acceptance in this country are the Otto-Hilgenstock, Simon-Carvès, Koppers, Semet-Solvay, Simplex, Coppée, and Hüssener.

Non-by-product and by-product ovens compared.—Prior to the establishment of the by-product coking process, the type of oven universally employed was that known as the beehive. This oven consists of a fireclay chamber, beehive shape in elevation and circular in plan, provided with a loose brick charging door at ground level, and with an exit flue in its crown for carrying the waste gases to the chimney. The coal is charged into the oven by spades, through the charging door, to a height of 2 feet 6 inches to 3 feet, is then ignited, and the charging door bricked up and plastered, a small hole 6 inches square being left for the admission of air. The surface of the coal burns and sets up distillation of the under layers, the evolved gases passing upwards and burning above the coal with the air drawn in at the door; this operation of distillation and immediate combustion proceeds until the whole of the volatile constituents of the coal have been evolved, which for a 10-ton charge occupies 70 hours. The coke is then quenched with water and withdrawn by rakes.

It will be seen that by this process, the whole of the volatile products, that is to say, benzols and ammonia together with the permanent gases, are burned immediately they are evolved within the coking chamber itself; further it is not possible to so regulate the combustion of these gases without burning a portion of the coke in addition; in actual practice, from 15 to 20 p.c. of the coke is burned to waste. For the reason, too, that the coke is quenched inside the oven, the temperature of the latter is lowered, so that before the next charge can be coked, considerable expenditure of heat is necessary to raise the oven to coking temperature. The removal of the coke by hand-rakes is also tedious and expensive.

With the object of overcoming the main drawbacks of the beehive oven, Coppée introduced a non-by-product retort of rectangular form, from which the coke could be discharged *en bloc* by a ramming machine and quenched outside the oven, thus expediting the operation and greatly increasing the yield. In Coppée's oven the gases evolved from the coal are drawn into flues in the side walls where they are burned, and in this way combustion within the coking chamber and loss of coke, as in the beehive oven, is avoided.

The by-product retort is built on the same lines as the Coppée, that is to say, it is a rectangular chamber heated by flues in the side walls, and the coke is discharged by a ramming machine; the essential point of difference lies in the fact that in the Coppée the whole of the gases containing the by-products are drawn immediately they are evolved into the side-wall heating flues, where they are burned; in the by-product retort, the gases and products are drawn from the oven through cooling and washing plant for the recovery of the tars, ammonia, and benzol, and the permanent gas only is burned in the flues after the said products have been extracted. In the Coppée, the whole of the permanent gas is burned in the heating flues; in the by-product oven, only one-half to two-thirds of the gas is utilised in the flues, the remainder being available for lighting or power purposes.

The following diagrams illustrate the essential differences in the three types of oven:

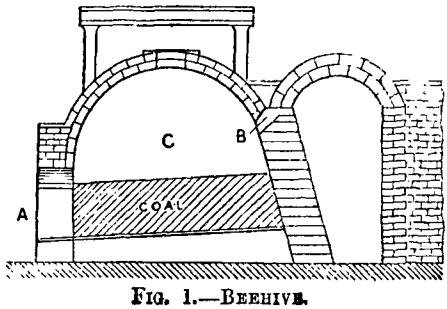


FIG. 1.—BEEHIVE.

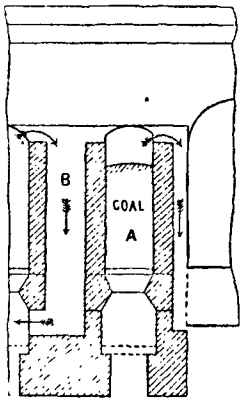


FIG. 2.—COPPÉE.

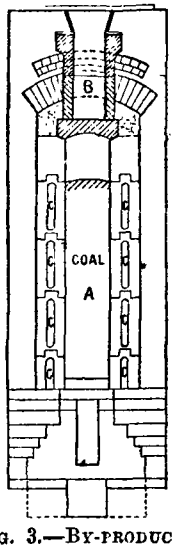


FIG. 3.—BY-PRODUCT RETORT.

It will be seen, therefore, that in addition to effecting the theoretical coke yield, and a large output, the by-product retort yields valuable by-products and a considerable yield of power or lighting gas. The value of products per 100 tons of coal at their present market value is as follows:—

	Gross value			Cost of recovery			Net value		
1 ton sulphate of ammonia .	£ 12	*s.* 0	*d.* 0	£ 2	*s.* 10	*d.* 0	£ 9	*s.* 10	*d.* 0
4·5 tons tar at 18*s.* .	4	1	0	0	9	0	3	12	0
300 gallons crude benzol at 5*d.* .	6	5	0	1	17	6	4	7	6
Per 100 tons of coal . . .							17	9	6

Per ton of coal = 3*s.* 5·9*d.*

The by-product process described in detail.—The by-product retort usually measures from 30 to 33 feet in length, from 5 feet 9 inches to 7 feet 6 inches in height, from 17 to 22 inches

TABLE SHOWING THE RETURN FROM CARBONISING A COAL CONTAINING 30 P.C. VOLATILE MATTER, *i.e.* A THEORETICAL COKE YIELD OF 70 P.C. IN THE THREE TYPES OF OVEN.

Beehive	Coppée	By-product retort
Combustion within coking chamber, quenching inside oven	Coking chamber heated externally by gas from which by-products not extracted: quenching outside oven	Coking chamber heated externally by gas from which by-products have been extracted: quenching outside oven
Yield of dry coke = 56 p.c.	70 p.c.	70 p.c.
„ tar —	—	4·0 to 4·5 p.c.
„ sulphate of ammonia	—	1·0 to 1·2 p.c.
„ benzol —	—	2·5 to 3·0 gallons of crude benzol testing 62 p.c. at 120° per ton of coal
Waste heat— In most cases not utilised but approximately equal to 0·75 ton of water evaporated per ton of coal carbonised	Always utilised: equal to 1 ton of water per ton of coal carbonised	Always utilised: equal to 1 ton of water per ton of coal carbonised. Surplus gas if required for other purposes than steam raising, *e.g.* gas engines or illumination, 3000 to 5000 cubic feet per ton of coal
Amount of coke produced per oven per week = 7 to 10 tons	24 to 26 tons	24 to 26 tons

in width, and is built in batteries of from 25 to 60 ovens, capable of carbonising from 100 to 350 tons of coal per day. Each oven is provided with cast-iron or rolled-steel doors at each end, lifted by a small crane whenever an oven is discharged, and with three holes in the roof through which the coal is charged into the oven from the charging hoppers; a fourth hole is provided, through which the gases are led to an ascension pipe from which the gases pass to the by-product plant. The oven linings and combustion flues are constructed of silicious firebricks containing from 80 to 84 p.c. of silica, from 14 to 18 p.c. of alumina, and 2 p.c. of fusible constituents (iron oxide, lime, magnesia, and the alkalis). The design of the heating flues constitutes the main difference between the various types of oven; the Simon-Carvès, Semet-Solvay, Hüssener, and Simplex containing horizontal flues; the Otto-Hilgenstock, Otto-Hoffmann and Koppers prefer vertical flues (Figs. 4 and 5). In all cases the air required for the combustion of the gas in the heating flues is preheated either by passing it through recuperators in which it travels through a system of flues situated alongside the waste gas flues of the oven, or through regenerators similar to those employed in open-hearth steel furnaces, where the hot waste gases and air are alternately taken over the same surface (Fig. 6). Where a large supply of surplus gas is desired from a coking plant, the regenerative method of preheating the air is to be preferred, since it is more effective and less gas is required for heating the flues; the amount of surplus gas available from a Lancashire coal containing 30 p.c. of volatile matter, may be taken at 2000 cubic feet per ton, where recuperative heating is employed, and 5000 cubic feet per ton where regeneratives are used.

The coal is generally charged into the oven through the crown from small hoppers, carrying the coal on rails from the storage bunker, the coal flowing into the oven being levelled by hand-rake or levelling machine. In cases where the coal employed is not of a strongly coking character, the fuel is stamped into a solid cartridge in a compressing machine and charged into the oven *en bloc* through the end doorway. The coke is discharged from the oven by a ram, generally electrically driven; often the levelling machine or compressor is built on the same carriage as the ram, and driven by the same motor. The coke is received from the ovens on a sloping bench, where it is quenched with water, and from which it slides into railway trucks, furnace barrows, or a conveyor. The heating flues of each oven discharge into a common flue, which leads the waste gases in the case of recuperator types to steam boilers; with regenerator-ovens, the gases are led direct to the chimney stack. The gases distilled from the coal collect above the level of the fuel and pass forward to the ascension pipe or stand pipe, which delivers the gas into the tar or hydraulic main, which receives the gases from the entire battery. A valve or damper is provided on each ascension pipe for shutting off each oven whilst the latter is being discharged and recharged. In the tar or hydraulic main the heavier tars or pitches are deposited, and in the 'dry' types of main, it is necessary to pump the thinner tars made at a later stage of the cooling, through the main to clear the pitch and prevent stoppages. From the main the gases are drawn by an exhauster (either steam or electrically driven), a Root's blower, or some form of aspirator, through coolers. These coolers are either plain pipes or cylinders offering a large amount of atmospheric cooling surface, or are water-cooled chambers; in these condensers, the bulk of the remaining tar, together with the greater proportion of the ammonia liquor, is precipitated.

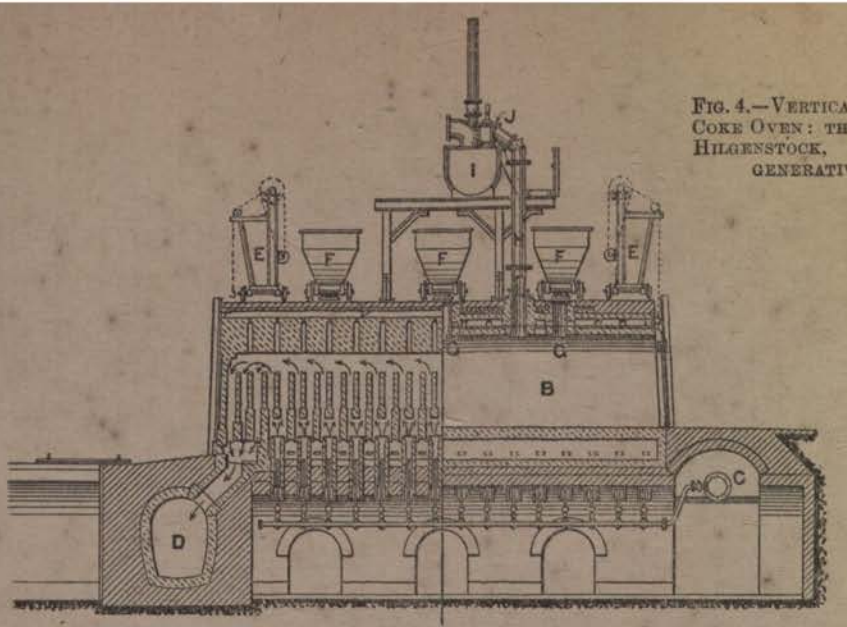
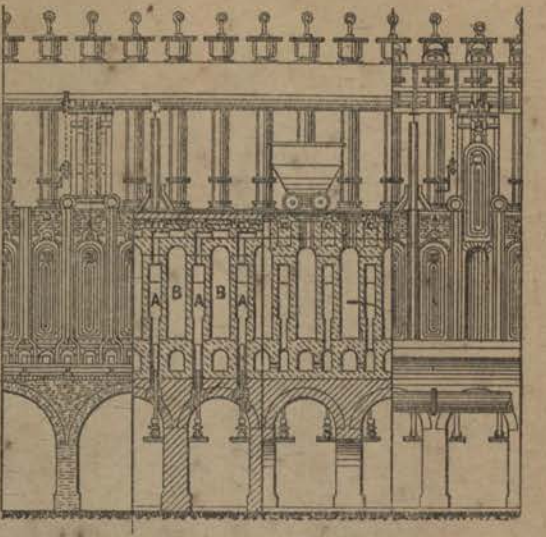


FIG. 4.—VERTICAL-FLUED COKE OVEN: THE OTTO-HILGENSTOCK, NON-REGENERATIVE.



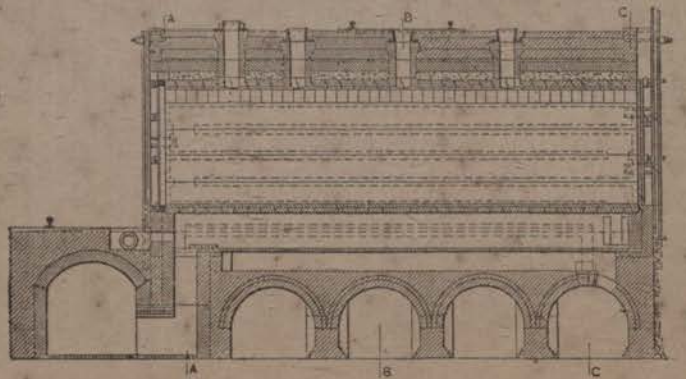


FIG. 5.—HORIZONTAL-FLUED COKE OVEN: THE SEMET-SOLVAY, NON-REGENERATIVE.

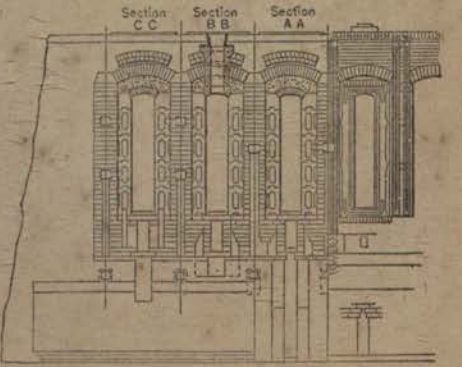


FIG. 5A.—SECTION THROUGH SEMET-SOLVAY OVEN.

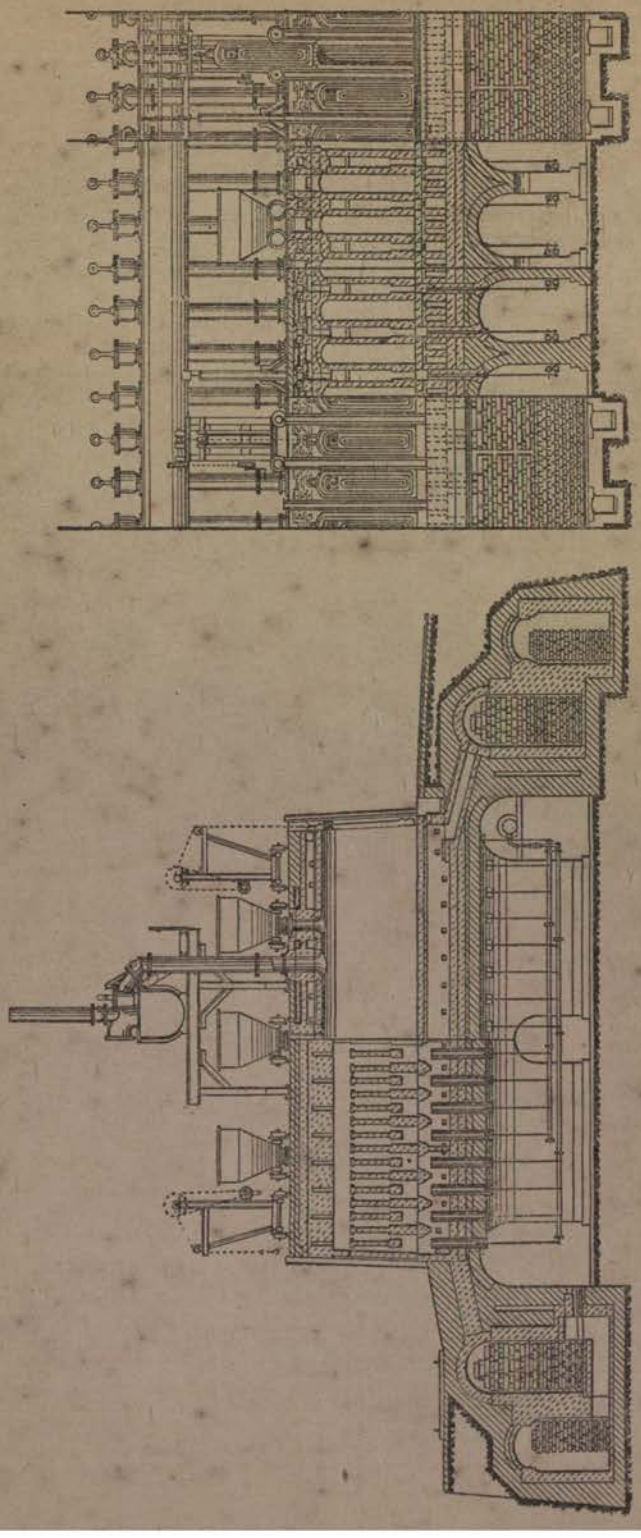


FIG. 6.—REGENERATIVE VERTICAL-FLUED COKE OVEN: THE OTTO-HILGENSTOCK.

From the condensers, the gases pass into the exhauster or aspirator, which then delivers them at a pressure into a tar-fog extractor. This vessel is employed to remove the last traces of tar which exist in the gas in an extremely fine state of division, and which no amount of cooling would remove. The tar extractor, of which the Pelouze Andouin and Livesay are types, operates by dividing the gas into numerous thin streams by means of very small gas passages, the agglomeration and removal of the tar particles being effected by the wire drawing and friction thus afforded.

From the tar catcher the gases pass into the ammonia scrubber, where the last of the ammonia not recovered by the condensers is removed by contact with weak ammonia liquor and water. The types of ammonia scrubber generally employed are similar to those employed at gas works, and are either of the tower or rotary form. In the tower scrubber, the gases pass upwards through a mass of coke or other open material, meeting a downward current of water or ammonia liquor pumped in at the top. In the rotary scrubber, the gas is caused to impinge on revolving brushes or circular wooden screens, which dip into the water or liquor in the lower half of the vessel, and pass upwards

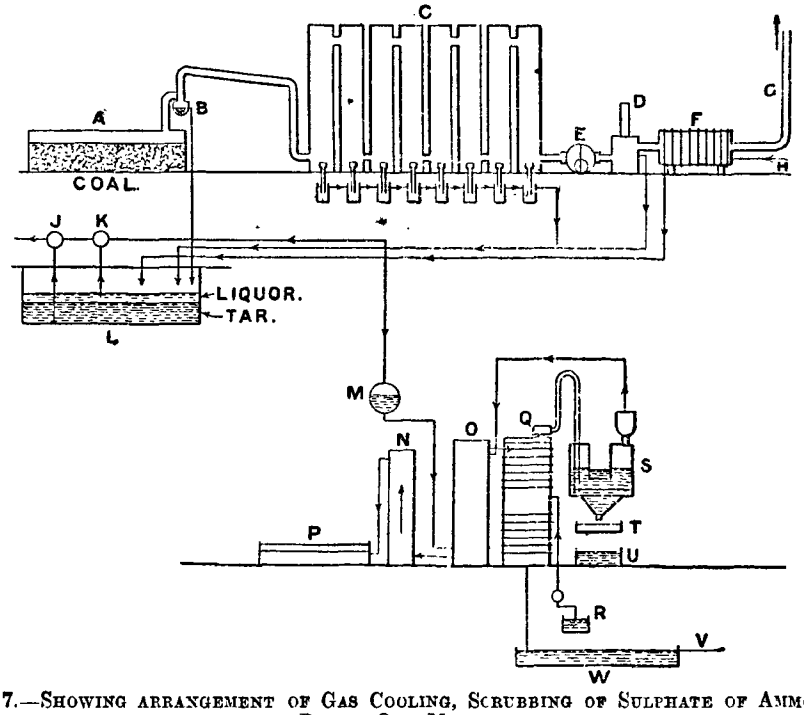


FIG. 7.—SHOWING ARRANGEMENT OF GAS COOLING, SCRUBBING OF SULPHATE OF AMMONIA PLANT, OLD METHOD.

A, Oven.
B, Hydraulic main
C, Condensers or coolers.
D, Tar catcher (Pelouze).
E, Exhauster.
F, Scrubber.
G, Return main to ovens.
H, Liquor feed to scrubber.
J, Tar pump to store.
K, Liquor pump to sulphate plant.
L, Tar and ammonia-liquor tank.
M, Liquor feed to still.
N, Cooler for sulphate plant waste gases.
O, Superheater.
P, Purifiers for sulphate plant waste gases.
Q, Ammonia still.
R, Lime feed to still.
S, Saturator.
T, Sulphate draining table.
U, Mother liquor well.
V, Spent liquor outlet.
W, Spent liquor settling tank.

with wet surfaces into the upper half of the scrubber, where the gas is circulating, and solution of ammonia is attained. The gas then passes forward to the benzol scrubber, which is constructed on similar lines to that employed for ammonia removal, creosote or anthracene heavy oil being employed for the solution and recovery of the benzol vapour.

The gas having been freed from its tar, ammonia liquor, and benzol, is then passed forward to the ovens, where it is fed into the heating flues, the surplus being passed forward to boilers, gas engines, or gas holder.

The tars and ammonia liquors made in the hydraulic main, condensers, tar catchers, and ammonia scrubber are collected and run into separators or tanks, where the denser tar settles to the bottom, is withdrawn and despatched to the tar stores. The liquors which remain above the tar are run off to the sulphate of ammonia plant, where the liquor is pumped into overhead store tanks, whence it is allowed to flow by gravity through a preheater (heated by the waste gases from the sulphate plant), and thence into a distilling column, where it flows downwards, meeting in its travel an upward current of steam, which liberates the free or combined ammonia. In the lower half of the still, milk of lime is mixed with the liquor for the liberation of the ammonia from the fixed

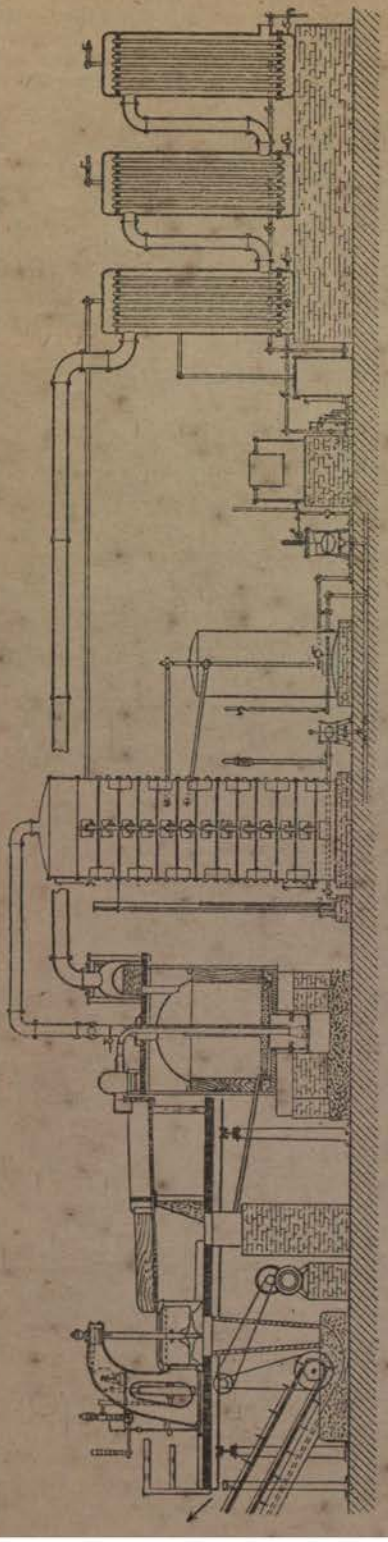


FIG. 8.—SULPHATE OF AMMONIA PLANT.

salts; the whole of the ammonia, together with steam, sulphuretted hydrogen, carbonic acid, and hydrocyanic acid, pass upwards through the still and into a lead-lined vessel called the saturator, containing sulphuric acid. The ammonia combines with the acid to form ammonium sulphate, which, when the liquor in the bath becomes saturated, crystallises out and is removed either by copper scoops, a valve, or by steam injector. The sulphuretted hydrogen and other gases pass from the saturator to the preheater, where they serve to heat the liquor passing to the still; thence the gases travel to a condenser where they are cooled, and afterwards to purifiers where the sulphuretted hydrogen is removed by oxide of iron. The waste liquors, which should not contain more than 0·01 p.c. ammonia, are run into the sewers or watercourses, and are a frequent source of trouble to the river boards. By the Otto-Hilgenstock method of by-product recovery, to be described later, the production of these waste liquors is entirely obviated.

The recovery of crude benzol from its solution in creosote or anthracene is effected in a distilling column somewhat similar to that employed for the recovery of ammonia from liquor, the heating of the solution of benzol in the absorbent being effected by wet steam assisted by dry steam. The vapours, steam, and benzol pass from the top of the still to a water-cooled coil, where they are together condensed, the condensates being separated by reason of their different densities. The grade of crude benzol thus obtained varies with the class of absorbent oil employed with creosote, 62 p.c. of the product distils at 120°, with anthracene the benzol is richer, 80 p.c. distilling at 120°. For the rectification of crude benzol, the product is washed successively with strongest oil of vitriol, water, and caustic soda, and redistilled.

Development in by-product recovery.—Two successful attempts have been made to simplify the old system of treatment of coke-oven gases for the recovery of ammonia, viz. the inventions of the Koppers and Otto-Hilgenstock Coke Oven Companies. Koppers treats his gases by the old system up to the point of the tar-fog extraction. He then reheats his tar-free gas by passing it in pipes surrounded by the hot gases coming from the ovens in an apparatus called a heat exchanger, and then passes the heated gas direct into a sulphate saturator, into which is likewise passed the ammonia from the liquor made in the condensers, which is distilled in an ordinary ammonia still. In short, Koppers abolishes the usual ammonia scrubber and substitutes the sulphate saturator, thus making his sulphate direct on the gas main (Fig. 9). By thus using the sulphuric acid in the saturator for scrubbing out the ammonia, Koppers dispenses with the water utilised in the old scrubber, thereby reducing the total amount of liquor produced, and effecting an economy in the amount of steam required in the ammonia distillation.

A far more extensive simplification is effected by the invention of the Otto-Hilgenstock Co. of Dahlhausen, who dispense entirely with the old condensing plant and remove the tar from the gases by means of a tar spray at a temperature above the dew-point of the liquors. The

tar-free gases then pass direct into a saturator, where the whole of the ammonia is caught by sulphuric acid. The gases issuing from the saturator still contain their liquors in steam form, and the whole passes forward to the oven-flues, and the offensive and troublesome waste liquors are thus got rid of. The Otto invention, by abolishing the condensing plant, liquor tanks, ammonia stills, lime mixers, and pumps, waste liquor tanks, &c., effects a great economy in ground space. It likewise saves nearly the whole of the steam required to distil the ammonia liquor

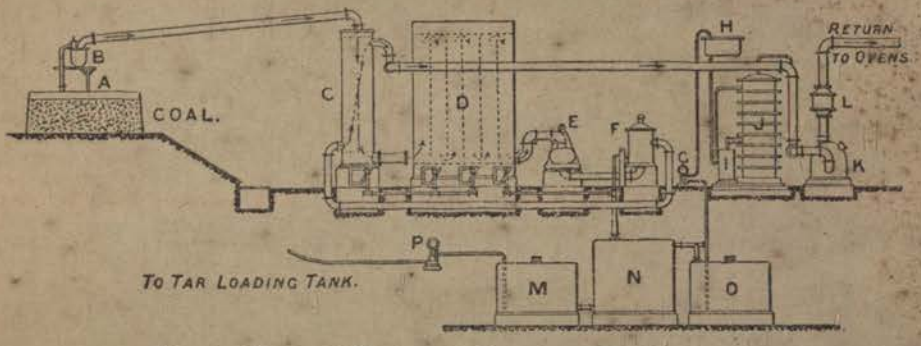


FIG. 9.—KOPPERS' BY-PRODUCT RECOVERY PROCESS.

A, Oven.
B, Hydraulic main.
C, Heat exchanger.
D, Condensers.
E, Exhauster.
F, Tar extractor.
G, Liquor pump to still.
H, Feed tank to still.
I, Liming chamber.
J, Ammonia still.
K, Saturator.
L, Acid spray catch-box.
M, Tar store tank.
N, Tar of liquor receiving tank.
O, Liquor tank.
P, Pump delivering tar to railway trucks.

made by the old condensing process, and, by passing the whole of the ammonia through sulphuric acid, losses of ammonia, which are liable to occur in the old process of ammonia liquor distillation, are rendered impossible. The ammonium sulphate made by the Otto direct-recovery, tests from 25 to 25·5 p.c. of ammonia, and contains only the merest traces of tar, viz. 0·05–0·1 p.c. (Fig. 10, 11, and 12).

The utilisation of coke-oven gas.—The large amounts of surplus gas obtained from the by-product coking process are gradually being diverted from use under steam boilers to more economic forms of application, and regenerative

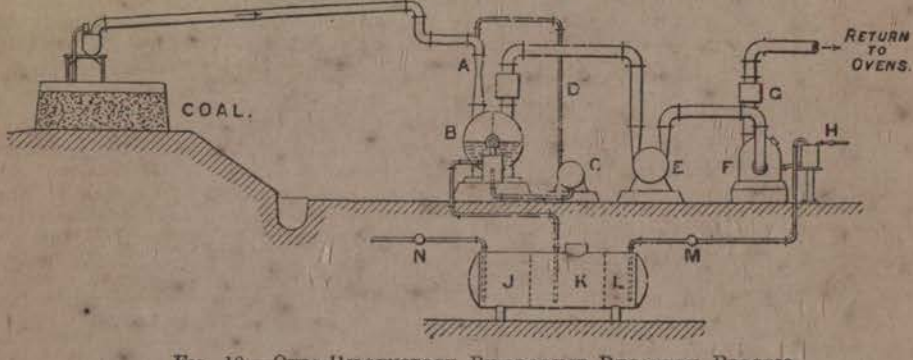


FIG. 10.—OTTO-HILGENSTOCK BY-PRODUCT RECOVERY PROCESS.

A, Tar spray.
B, Tar spray receiving tank.
C, Tar spray pump.
D, Tar spray feed pipe.
E, Exhauster.
F, Saturator.
G, Acid spray catch-box.
H, Mother liquor return pipe.
J, Tar store.
K, Tar spray overflow tank.
L, Condensing tank.
M, Pump delivering condensings to saturator.
N, Pump delivering tar to railway trucks.

ovens are now being erected as power stations, in addition to the facilities which they afford for economic coke manufacture and by-product recovery. At many collieries and iron works on the Continent, large gas-engine installations have been set down for the utilisation of coke-oven gas; and in England its use is being surely extended. The coke-oven plant erected by the Otto-Hilgenstock Coke Oven Co., for the Skinningrove Iron Co. Carlin How, Yorkshire, provides sufficient surplus gas to develop 7000 horse-power.

The use of coke-oven gas as a town's illuminant is likewise receiving attention, and with the development of the incandescent mantle, which requires gas of calorific rather than of candle value, coke-oven gas comes into the category of ordinary coal gas. In the year 1910 Parliament granted powers for the supply of gas from Lord Ellesmere's Brackley coke

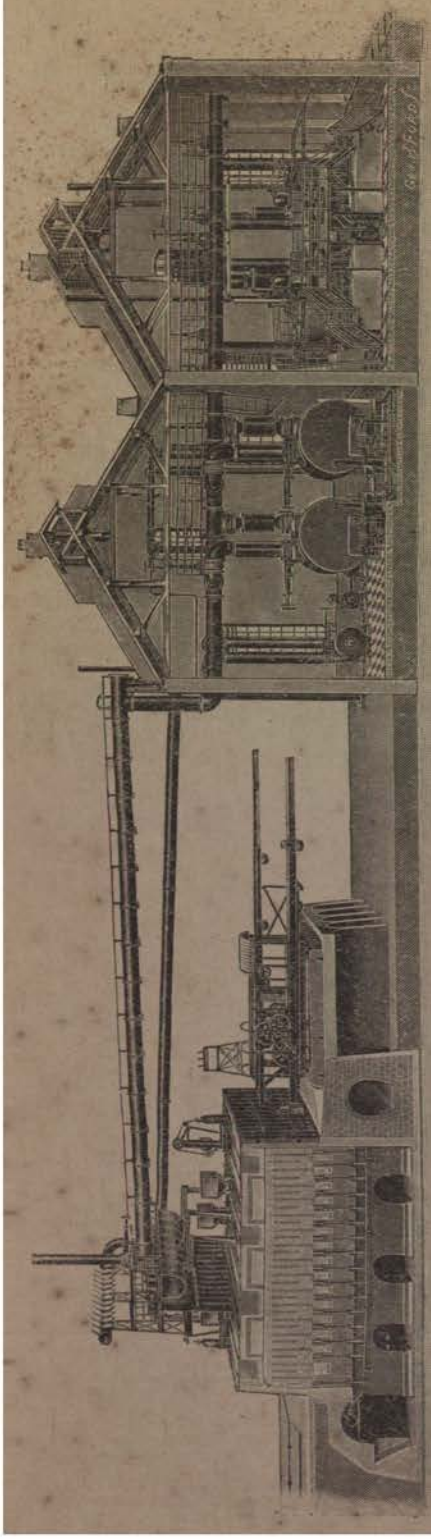


FIG. 11.—MODEL OF OTTO-HILGENSTOCK SYSTEM: PLANT ERECTED FOR THE SKINNINGROVE IRON CO.

ovens to the urban district of Little Hulton, the guarantees of quality and purity of the product being identical with the gas supplied to the Metropolis, that is to say, the gas has a minimum illuminating power of 14 standard sperm candles, tested by the Metropolitan No. 2 Argand burner, and a calorific guarantee of 550 B.T.U. gross. The average composition of the gas is: CO_2, 2·5; O, 0·3; C_2H_4, 3·8; C_6H_6 &c., nil; CO, 7·0; CH_4, 31·0; H, 49·0; N, 6·4. E. B.

COLATANNIN *v.* TANNINS.

COLCHICINE *v.* VEGETO-ALKALOIDS.

COLCHICUM. *Meadow saffron.* (*Colchique*, Fr.; *Herbstzeitlose*, Ger.) The corm or seeds of *Colchicum autumnale* (Linn.), (Bentl. a. Trim. 288). This plant is found in meadows and pastures throughout Europe, where its crocus-like flowers, usually of a lilac hue, make their appearance in September and October.

Colchicum is a poisonous drug long known to medicine. It has been subject to repeated investigation with a view to isolate its active constituent or constituents. Among earlier inquiries are those of Melander and Moretti, 1810 (Bull. Pharm. 2, 217); Stoltze, 1818 (Berz. J. 19, 107; 20, 135); Pelletier and Caventou, 1820 (Ann. Chim. Phys. [2] 14, 69; J. Pharm. Chim. 6, 364); Buchner, 1832 (Rep. Pharm. 43, 376). Besides substances common to plants, such as starch, gum, cellulose, sugar, oil, resin, &c., the older workers detected a bitter extractive possessing physiological activity, and Pelletier and Caventou regarded it as containing gallate of veratrine. Geiger and Hesse, in 1833 (Annalen, 7, 274), showed, however, that the bitter alkaloidal compound, which they describe as crystalline, has properties quite distinct from veratrine, and they gave it the name *colchicine*. It is faintly alkaline, is sparingly soluble in water, but dissolves readily in alcohol or chloroform, the latter extracting it from its aqueous solution; the dry compound strikes a deep violet to blue colour with concentrated nitric acid, and its aqueous solution is precipitated brown by tincture of iodine, yellow by platinum chloride solution, and white by tannic acid. The corm yields less than 0·1 p.c. of colchicine. The subject is further studied by Aschoff (Arch. Pharm. [3] 89, 4); Bley (*ibid.* [3] 89, 18); Hübschmann (*ibid.* [3] 92, 330); and Oberlin (Ann. Chim. Phys. [3] 1, 108). The last-mentioned observer, by the action of dilute acids, succeeded in breaking up colchicine into a new alkaloid *colchiceïne* and other products. This compound was obtained in colourless laminæ or needles, sparingly soluble in cold, more so in boiling water, readily in alcohol or chloroform, insoluble in ether or benzene. Full directions for extracting colchicine from the crude drug, and its conversion into colchiceïne are given by Hertel (Pharm. Zeit. 1881, 245), who observes that when exposed to the air, colchiceïne gives off ammonia and water, and is converted successively into two resins: *α-colchico-resin* $C_{51}H_{60}N_2O_5$ (?), and *β-colchico-resin* $C_{34}H_{39}NO_{10}$ (?). These resins are formed in the officinal wine of colchicum, but are not indications of therapeutical deterioration, for they possess equal medicinal value with the alkaloid from which they are derived.

Important contributions to the chemistry of colchicine and colchiceïne have more recently been

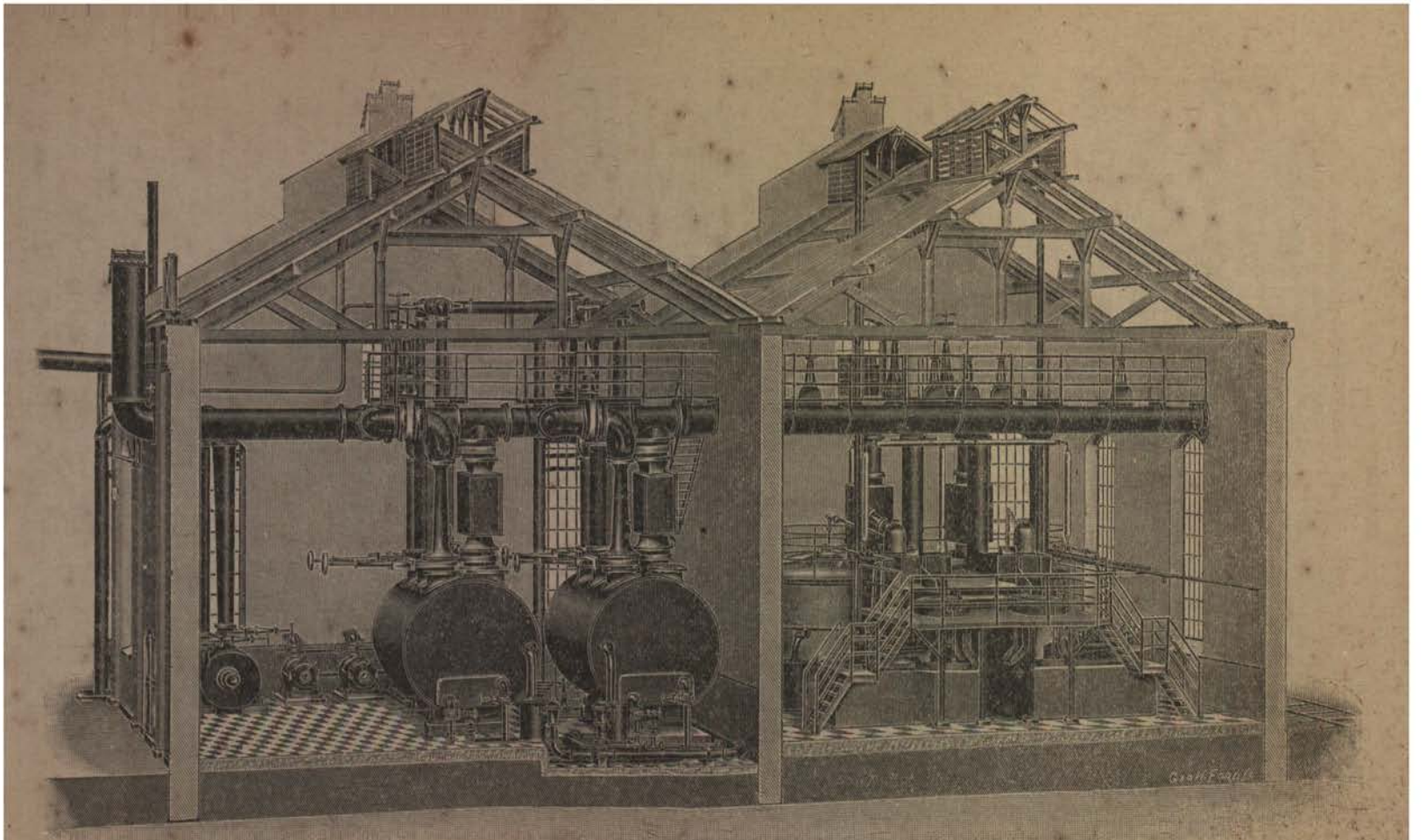


FIG. 12.—OTTO-HILGENSTOCK DIRECT RECOVERY PLANT ERECTED FOR THE SKINNINGROVE IRON CO.

made by Zeisel (Monatsh. 4, 162; 7, 557; 9, 1; 9, 865). After reviewing previous work, this observer assigns to colchicine the formula $C_{22}H_{25}NO_6$. It melts at about 145° and forms a characteristic crystalline compound with chloroform $C_{22}H_{25}NO_6,2CHCl_3$ (Houde, Compt. rend. 98, 1442; Zeisel, *ibid.* 98, 1587). Colchicine is slightly basic, forming a *gold salt* $(C_{22}H_{25}NO_6)HAuCl_4$. *Methyl colchicine* $C_{22}H_{24}MeNO_6$ has also been obtained. In the conversion of colchicine into *colchiceïne* $CH_3{\cdot}OH$ is evolved, and the new alkaloid has the composition $(C_{21}H_{23}NO_6)_2,H_2O$. It melts at 139°–141°, loses its water of crystallisation at 140°–150°, becoming solid, and on further application of heat the anhydrous alkaloid softens at 161° and melts at 172°. Colchicine appears, therefore, to be a methylcolchiceïne. When colchicine is treated with concentrated hydrochloric acid, the reaction does not stop with the formation of colchiceïene by the displacement of one methyl group; but this is accompanied by that of an acetyl radicle, leaving an *acid* $C_{19}H_{21}NO_8$ or $(C_{18}H_{20}NO_3)COOH$. In the further progress of the reaction, this compound loses another methyl group, giving rise to a second *acid* $(C_{17}H_{18}NO_3)COOH$, and finally by the displacement of two additional methyl groups, *colchicinic acid* $(C_{15}H_{14}NO_3)COOH$ is obtained. The second acid described is therefore *dimethyl colchicinic acid*, and the first acid *trimethyl colchicinic acid*; whilst colchiceïne is regarded as *acetyl trimethyl colchicinic acid*, and colchicine, which does not possess acid properties, as the methyl ester of colchiceïne. Colchiceïne is basic, forming the *gold salt* $C_{21}H_{23}NO_6{\cdot}HAuCl_4$, but it is also acid, or at least phenolic, giving rise to the *copper derivative* $(C_{21}H_{22}NO_6)_2Cu,5H_2O$. The acid property of colchiceïne is further apparent in the readiness with which it combines with alkalis. By treatment with methyl iodide and sodium methoxide colchiceine may be converted into colchicine.

Colchicine has also been found to occur in other varieties of colchicum (Albo, Arch. Sci. Phys. Nat. Geneva, 1901, iv. 12, 222).

Colchicum is a favourite remedy in the treatment of gout and rheumatism. It acts as an irritant of the alimentary canal and kidneys, being a purgative and diuretic, and in large doses these symptoms become more and more violent until a fatal result follows. The action is cumulative (Mairet and Combemerle, Compt. rend. 104, 439, 515). *Post-mortem* examination of the stomach contents by treatment with alcohol, and purification of the extract obtained by fresh treatment with alcohol or with chloroform, and then the application of the nitric acid and other tests, may be adopted in cases where death is supposed to have been caused by colchicum. (*Cf.* Dannenberg (Arch. Pharm. [3] 8, 411; 10, 97), and Van Geldern (*ibid.* [3] 9, 32); Obolonski (Zeitsch. anal. Chem. 29, 493).)

Flückiger (Pharm. J. [3] 7, 372) recommends the colour reactions which an alcoholic extract of colchicum corms gives with mineral acids as a delicate means of detecting those acids. (For detection and estimation of colchicum, *see* also Kremel, Zeitsch. anal. Chem. 29, 727); Barillot (Bull. Soc. chim. [3] 11, 514); Prescott and Gordin (Chem. Zentr. 1900, ii. 784).) A. S.

COLCOTHAR. The reddish-brown residue of ferric oxide obtained in the manufacture of fuming oil of vitriol from iron sulphate.

COLEMANITE. A hydrated calcium borate $Ca_2B_6O_{11},5H_2O$, containing 50·9 p.c. boron trioxide. It is found in California at Death Valley in Inyo Co., and the Calico district in San Bernardino Co.; and although not discovered until 1882 and 1883, is now of some importance as a material for the preparation of borax and boracic acid. Cavities in the massive, white material are lined with beautiful, water-clear crystals with a profusion of brilliant facets; these are monoclinic, with a perfect, pearly cleavage parallel to the plane of symmetry. They are considerably harder (H. 4–4½) than borax; sp.gr. 2·42. The mineral forms, together with other borates and borosilicates, a bed 7 to 10 feet in thickness in sandstones and clays.

The compact minerals, *priceite* from Oregon and *pandermite* from Asia Minor, have very nearly the same composition, and they may be regarded as impure, massive varieties of colemanite. These also are mined as borates.

L. J. S.

COLLIDINE *v.* BONE OIL.

COLLIN. A preparation made by heating a solution of hide powder or gelatin with caustic soda and neutralising with acetic acid. Used in the analysis of tannin and tanning materials (Parker and Payne, J. Soc. Chem. Ind. 1904, 648; Wood and Trotman, *ibid.* 1904, 1071).

COLLODION *v.* PHOTOGRAPHY.

COLLODION COTTON *v.* EXPLOSIVES.

COLLOIDS. In 1861 Graham pointed out that substances which crystallise readily from water are characterised by a high power of diffusion and by the ability to pass through animal or vegetable membranes; substances, on the other hand, which cannot easily be obtained in the crystallised condition are characterised by a low power of diffusion and by inability to pass through animal or vegetable membranes. Graham termed substances of the first class, such as sucrose or sodium chloride, *crystalloids*; and those of the second class, such as starch, gum, or albumin, *colloids*. The separation of a colloid from a crystalloid is effected by dialysis, a process based on the inability of a colloid to pass through parchment or other membrane.

At the present time, the term 'colloid' is used in a sense somewhat different from that in which Graham employed it, and is to be interpreted as referring, not so much to a particular class of substances, as to a condition which a large number of chemical compounds may be made to assume. A 'colloidal solution,' therefore, is not necessarily a solution of a colloid (in Graham's sense); it is a solution the properties of which are, in many respects, similar to those of, say, a gum arabic solution, although the dissolved substance may be quite outside the class which Graham termed 'colloids'; it may be, for instance, ferric hydroxide, arsenious sulphide, or platinum.

Osmotic properties of colloidal solutions.—The osmotic pressure of a colloidal solution is extremely low. According to Duclaux, for instance, the osmotic pressure of an 8·86 p.c. ferric hydroxide solution is only 22·6 cm. of

water, which is about equal to the pressure given by a solution of sucrose containing one-thirtieth of a gram in 100 grams of water. It has, indeed, been suggested that the osmotic pressures which have been observed for colloidal solutions are due, not to the colloids themselves, but to small quantities of electrolytes associated with the colloids. While it is certainly true that the removal of the last traces of electrolytes from a colloidal solution is no easy matter, and that electrolytes are extremely active material from the osmotic point of view, still the most recent investigations indicate that colloidal solutions do possess a definite, if small, osmotic pressure. It appears, however, that the osmotic pressure of a colloidal solution is not completely defined, as is that of a crystalloidal solution, by concentration and temperature. Thus Moore and Roaf have found (Biochem. J. 1906, 2, 34) that the osmotic pressure of a given gelatin solution at a given temperature depends, to some extent, on its previous history, while Lillie has found (Amer. J. Physiol. 1907, 20, 127; *see also* Bayliss, Proc. Roy. Soc. B, 1907, 81, 269) that the osmotic activity exhibited by the colloid itself is modified by the presence of electrolytes in a remarkable degree. Concentration and temperature, therefore, are not the only factors which determine the osmotic pressure of a colloidal solution.

The depression of the freezing-point and the elevation of the boiling-point of water by a dissolved substance are quantitatively related to the osmotic pressure of the solution, and, like the latter, may be made the basis for a determination of the molecular weight of the solute. The freezing-point and boiling-point of a colloidal solution are, however, very slightly different from those of water itself, and the experimental error of the determination of the molecular weight of the colloid by this method is relatively large. In view, further, of the fact that the osmotic activity of a colloid depends on other factors than those of concentration and temperature, it is obvious that the values for the molecular weight of a colloid deduced from its effect on the freezing-point or boiling-point of water have a very limited significance. Such values have reference only to the particular condition of the colloid at the time of the determination.

Colloids in an electric field.—In 1892 Linder and Picton observed (Chem. Soc. Trans. 1892, 61, 148) that when two wires, connected with the terminals of a battery, are placed in a colloidal solution of arsenious sulphide, this substance is attracted by the positive pole and is gradually transported thither. Ferric hydroxide in colloidal solution is, on the other hand, attracted by the negative pole. It appears, therefore, that the particles of colloidal arsenious sulphide carry a negative charge, whilst those of colloidal ferric hydroxide carry a positive charge. Other colloids are similarly found to carry a definite charge; thus chromium and aluminium hydroxides, methylene blue, Bismarck brown and hæmoglobin, are electropositive; tannin, caramel, starch, platinum, gold, and indigo are electronegative. Very significant in this connection is Hardy's observation (J. Physiol. 1899, 24, 288), that protein is electronegative in an alkaline medium, but electropositive in an acid medium. A reversal of the electric charge on a colloid has been observed in other cases also (*see* Burton, Phil. Mag. 1906, 12, 472).

Colloidal solutions and suspensions.—The behaviour of substances in colloidal solution, when exposed to the action of an electric force is very similar to the behaviour of suspensions in the same circumstances. When wires connected with the terminals of a battery are immersed in suspensions of quartz powder, gum mastic, or shellac, the suspended particles move towards the positive pole. These are facts which suggest a close relationship between colloidal solutions on the one hand, and mechanical suspensions on the other. This view is strongly supported by various other lines of evidence. Thus the majority of colloida, solutions exhibit the Tyndall phenomenon, *i.e.* the opalescence which is observed when a powerful beam of light is passed through a fluid medium containing definite suspended particles. Further, the ultramicroscope, devised by Zsigmondy and Siedentopf, makes it possible to detect the individual particles in colloidal solutions, even when the most powerful microscope fails to reveal any trace of heterogeneity. There are therefore good grounds for the view that there is a close relationship between colloidal solutions and mechanical suspensions.

There are, however, cases on record in which colloidal solutions, even when examined with the ultramicroscope, have been found free from distinct particles. On the other hand, evidence has been adduced (Lobry de Bruyn, Rec. trav. chim. 1904, 23, 155, 218) showing that solutions of a heavy crystalloid, such as sucrose, are non-homogeneous. Hence it is evidently impossible to draw a hard-and-fast line of division between colloidal and crystalloidal solutions, so far at least as the size of the solute particles is concerned. The smallest particle that can be detected with the ultramicroscope under the most favourable conditions is about 5×10^{-6} mm. in diameter, and it is estimated that the size of an ethyl alcohol molecule is $0{\cdot}4 \times 10^{-6}$ mm., so that in any case the interval between the region of colloidal solutions and that of average crystalloidal solutions is not great. So far as the size of the individual particle is concerned, colloidal solutions are intermediate between mechanical suspensions on the one hand and crystalloidal solutions on the other, but the inadvisability of regarding these three classes as absolutely distinct is clearly indicated by the fact that it is possible to prepare solutions of one and the same substance of various degrees of heterogeneity. Linder and Picton were able to prepare different 'grades' of arsenious sulphide solution; and in deciding whether a given solution of arsenious sulphide is a colloidal solution or merely a mechanical suspension, the verdict will depend on the criterion of heterogeneity which is employed.

The particles which are detected in a colloidal solution with the help of the ultramicroscope are seen to be in a state of constant motion—a phenomenon essentially the same as the Brownian movement exhibited by gamboge or fat particles suspended in water. The finer the particles the more rapid is their movement, and a study of the relationship between the size of the particle and its rate of movement has led to a calculation of the rate at which a particle of

molecular size would move. The value so calculated is in good agreement with the value deduced from the kinetic theory, and this agreement is regarded as amounting to a definite proof of the kinetic nature of heat.

Separation of colloids from their solutions.—Substances in colloidal solution pass through the finest filter paper, but if the close relationship between mechanical suspensions and colloidal solutions is borne in mind, it will be seen that the question whether filtration can be effected in the latter case as in the former reduces itself to the question whether filters with sufficiently small pores can be procured. The most successful attempts that have been made to solve this problem depend on the impregnation of a suitable supporting medium with a colloid such as gelatin or collodion. Filter paper, for instance, may be soaked in gelatin solution and then hardened with formaldehyde, or impregnated with a solution of collodion in glacial acetic acid and then dipped in water. As the concentration of the impregnating gelatin solution is increased, the permeability of the filter to colloids diminishes, so that a series of graded filters can be prepared which may be employed to sort out a number of colloidal solutions, according to the size of particles they contain (*see* Bechhold, Zeitsch. physikal. Chem, 1907, 60, 257). It is noteworthy that these 'ultra-filters,' as they are called, may be employed to separate oil-water emulsions (*see* Hatschek, J. Soc. Chem. Ind. 1910, 29, 125).

Another method of separating a colloid from its solution is to precipitate the colloid and then filter off in the ordinary way. It is found that in relation to precipitating or coagulating agents, the substances which form colloidal solutions may be divided into two classes—the one class resembling suspensions, the other behaving more like crystalloid substances. The colloids belonging to the first class are known as 'suspension colloids,' and they give non-viscous solutions which are coagulated by small quantities of electrolytes; these colloids are known also as 'non-reversible,' for when once they have been separated they do not again pass into solution by mere contact with water; their solutions can be obtained only by indirect methods. The colloids belonging to the second class are known as 'emulsion colloids,' and they give viscous solutions which are not readily coagulated by electrolytes; they are also termed 'reversible' colloids, because, even if separated from solution by any means, they will again pass into solution on mere contact with water.

The coagulation of suspension colloids, such as arsenious sulphide or ferric hydroxide, is brought about by extremely small quantities of electrolytes. When experiments are made to determine the minimum concentration of various electrolytes required to precipitate colloidal arsenious sulphide, it is found that this minimum concentration is of the same order for all salts containing cations of equal valency; the higher the valency of the cation, the smaller is the concentration of the electrolyte required to bring about coagulation. In relation to colloidal ferric hydroxide, on the other hand, the coagulating power of a salt is mainly determined by the valency of the negative ion; the valency of the cation is relatively unimportant. The contrast in this respect between colloidal arsenious sulphide and colloidal ferric hydroxide is very interesting in view of the fact that the colloid particles of arsenious sulphide are negatively charged, while those of ferric hydroxide are positively charged. The full significance of this was first emphasised by Hardy (Zeitsch. physikal. Chem. 1900, 33, 385), who formulated the rule that the ion of an electrolyte which determines the coagulation of a colloidal solution is the one which has a charge opposite in sign to that on the colloid particles. The validity of this rule has been extensively confirmed. The 'coagulum' or 'hydrogel' obtained when a solution of a suspension colloid is precipitated by a salt contains some of the acidic or basic part of the salt. Thus the coagulum obtained when colloidal arsenious sulphide is precipitated with barium chloride, is found to contain barium, and in proportion as the coagulum retains barium, the filtrate becomes acid. The barium cannot be removed by continued washing with water, but may be replaced by an equivalent quantity of another metal by digesting the coagulum with a solution of the chloride of this metal.

If, as suggested by the facts just mentioned, the coagulation of a suspension colloid by a salt is essentially a neutralisation of electric charges, it may be expected that colloids of opposite electrical sign will precipitate each other. In harmony with this, it is found that while no coagulation occurs when colloidal solutions ('hydrosols') of the same electrical sign are mixed, precipitation immediately follows the addition of the solution of a positive colloid to the solution of a negative colloid, unless one of the colloids is in very large excess. For a certain proportion of the colloids, the precipitation of both is complete, but as the quantities deviate from this optimal ratio, precipitation is increasingly incomplete. The precipitation of egg albumin by solutions of various complex acids—*e.g.* molybdic, tungstic, and tannic acids —furnishes an example of the mutual coagulation of two colloids. Metaphosphoric acid, too, forms a pseudo-solution or hydrosol which precipitates albumin, while the crystalloidal orthophosphoric acid has no such effect.

The separation of emulsion colloids, such as serum protein, from their solutions, may also be effected by the addition of electrolytes, but the process is essentially distinct from the corresponding precipitation of suspension colloids; it is not electrical in character. When a number of alkali salts are arranged according to their efficiency in precipitating emulsion colloids, the order is practically the same as when they are arranged according to their efficiency in salting out an organic compound from water or according to their power of lowering the solubility of gases in water. The precipitation of emulsion or reversible colloids by neutral alkali salts appears, therefore, to be closely allied to the process of 'salting out,' and this result of itself shows that solutions of reversible colloids approximate more closely to true solutions than do solutions of suspension colloids.

Not only are emulsion colloids themselves very slightly sensitive to electrolytes, but in presence of an emulsion colloid the precipitation

of a suspension colloid by salts is more or less inhibited. This is not due to an increase in the viscosity of the medium and consequent increase of resistance to sedimentation, for the protective effect is exhibited by quantities of the reversible colloid insufficient to cause any appreciable change in viscosity. It is probable that the emulsion colloid forms a thin envelope round each particle of the suspension colloid and so prevents the aggregation and subsequent flocculation of the particles.

Adsorption.—Reference has already been made to a difference of electrical potential as determining in some cases the relation between a colloid and its environment. There is, however, another factor which must be taken into account in the consideration of this question, and that is the relatively enormous surface of contact between the colloid and the surrounding medium. The evidence sketched in the foregoing paragraphs shows that a colloidal solution is really a two-phase system, consisting of a fluid medium in which are distinct suspended particles of extremely small size. Now, it is obvious that as a given quantity of matter is divided up more and more finely, its surface area increases regularly. The surface area, for instance, of a single sphere with a diameter of 1 mm. is 0·0314 sq. cm.; if the matter composing this sphere were broken up into a number of smaller spheres, each 0·0001 mm. in diameter, the total surface area of the spheres would be 314 sq. cm. It is evident, therefore, that in a colloidal solution with its fine suspended particles, there must be relatively a very large surface of contact between the colloid and its medium.

On the basis of the two-phase character of colloidal solutions and the large surface development of the colloid phase, the relation of colloids to each other and to various solid and dissolved substances may be regarded as being essentially of the nature of 'adsorption.' This term is used in reference to the observation that when a substance is introduced into a two-phase system, and provision is made for its distribution throughout the system, it is frequently found concentrated at the surface of one of the phases. The nature of this phenomenon will perhaps be best appreciated by contrasting it with cases in which the substance is distributed uniformly in each phase of the two-phase system. When iodine is shaken up with two immiscible liquids, such as water and carbon tetrachloride, a state of equilibrium is soon reached at which the concentration of the iodine is uniform throughout the aqueous phase, uniform also (but different) throughout the carbon tetrachloride phase. If c_1 is the concentration of iodine in the aqueous layer, and c_2 its concentration in the carbon tetrachloride layer, then c_2/c_1, the 'partition coefficient,' is found to be a constant, independent of the absolute values of c_1 and c_2. This is a rule applicable to the distribution of any substance between two immiscible liquids, provided the molecular condition of the substance is the same in each liquid. If, on the other hand, the molecular weight of the substance in the first liquid is n times its molecular weight in the second liquid, then c_2''/c_1 is a constant, independent of the absolute values of c_1 and c_2. If, conversely, the distribution of a substance between two liquids at various concentrations has been found to be such that c_2''/c_1 is a constant, the conclusion may be drawn that the molecular weight of the substance in the first liquid is n times its molecular weight in the second liquid.

The distribution of a substance in a two-phase system which consists, not of two immiscible liquids, but of a solid and a liquid, is generally quite different in character. When, for instance, acetic acid solutions of various concentrations are shaken up with carbon, a state of equilibrium is rapidly attained, and it is found that some of the acetic acid has been taken up by the carbon. If c_s and c_l represent the equilibrium concentrations of the acetic acid in the solid and the liquid phase respectively, then the experiments show that $c_s^{2\cdot35}/c_l$ is a constant. According to the foregoing paragraph, this would mean, on the assumption of a uniform distribution of the acetic acid throughout the carbon, that the molecular weight of acetic acid in the carbon must be less than half what it is in water. This conclusion must obviously be rejected, and the assumption of a uniform distribution of the acetic acid throughout the carbon is incorrect. The acetic acid must be concentrated at the surface of the carbon, a view supported by the rapidity with which equilibrium is established. The acetic acid is said to be 'adsorbed' by the carbon, and the phenomenon is termed 'adsorption.'

The distribution of a substance in a two-phase system where one of the phases is a solid with largely developed surface, is generally found to consist in an adsorption equilibrium. This is indicated, qualitatively, by the concentration of the substance in the solid phase increasing more slowly than its concentration in the liquid phase, and quantitatively by the validity of the formula c_s''/c_l=constant. In this way it has been shown, to quote one or two examples, that the taking up of gases by charcoal, the removal of arsenious acid from solution by freshly precipitated ferric hydroxide, and the dyeing of silk with picric acid and numerous other colouring matters, are all cases of adsorption. The complexes formed, although not due to chemical combination in the strict sense, and although lacking the characteristics associated with a definite chemical substance, are frequently referred to as 'adsorption compounds.' As van Bemmelen especially has shown, colloids in the form of hydrogels have a very marked power of adsorbing other colloids, crystalloids and water, and evidence is accumulating in favour of the view that the behaviour of colloids in solution towards other substances is also to be interpreted in terms of adsorption.

The question may be asked: Is there any physical reason for the concentration of a substance at the surface of one of the phases in a two-phase system, such as a colloidal solution undoubtedly is? The answer is that if surface tension considerations only are taken into account, then it follows on thermodynamical grounds that the most stable relation between the two phases of a colloidal solution is the one characterised by a minimum surface tension. Hence if the substance present in the solution lowers the surface tension of the solvent, that

substance will accumulate in the surface layer of the solution. That such spontaneous accumulations may occur in the surface layers of solutions has been shown by Ramsden (Proc. Roy. Soc. A, 1903, 72, 156), who observed the formation of solid or highly viscous coatings on the free surfaces of protein and many other colloidal solutions.

Bearing of colloid chemistry on technical problems.—The *rôle* played by colloids in the operations of applied chemistry is of great importance. In the manufacture of starch, cellulose, glue, leather, caoutchouc, artificial silk, paper, and photographic plates, colloids are involved, and a knowledge of the general behaviour of colloids throws much light on these and other industrial operations. Many dyes give colloidal solutions, and dyeing, in a large number of cases at any rate, depends on the adsorption of the colouring matter by the fibre. The relation between hide and tannin appears to be of the same description, and the investigation of the tanning process from this point of view shows the definite bearing which colloid and adsorption phenomena have on this operation. The problem of sewage disposal also is closely related to colloid chemistry, and it has been found practicable to retain the colloids of the sewage in the form of adsorption compounds. The tints of coloured glasses are frequently due to the presence of metals in the colloidal state. This is notably the case with gold ruby glass, which owes its colour to the presence of ultramicroscopic particles of the metal. Colloid chemistry has an important bearing, too, on agricultural chemistry. Many of the properties of soils—for example, permeability, absorptive power, and moisture content—depend more on the size of the constituent particles than on their chemical composition. The retention by the soil particles of materials of nutritive value for plants is closely related to the phenomenon of adsorption already discussed. Colloids are of importance further in connection with the pottery trade. Highly plastic clays behave like colloids, and the treatment of clay with a colloid, such as tannin, notably increases the plasticity of the material.

Reference has been made above to the protective action of emulsion colloids, and this phenomenon is of frequent occurrence. The presence of such colloids, generally and vaguely referred to as 'organic matter,' may altogether prevent the flocculation and precipitation of insoluble compounds. In presence of gelatin, for example, silver nitrate gives with sodium chloride only an opalescence which is not altered by filtration. This is a fact of the greatest importance in connection with photographic emulsions. Closely related to this phenomenon is the use of glues and gums as retarders in the setting of plaster of Paris, and the inclusion of such materials in mixtures which have for their object the prevention of scale in boilers. Detailed references to the bearing of colloid chemistry on technical problems will be found in a monograph, Die Bedeutung der Kolloide für die Technik (Dresden, 1909), by K. Arndt, and in a paper on Colloid Chemistry and some of its Technical Aspects, by J. Alexander (J. Soc. Chem. Ind. 1909, 28, 280). J. C. P.

COLLOTYPE *v.* PHOTOGRAPHY.

COLOCYNTH. *Bitter apple.* (*Coloquinte*, Fr.; *Koloquinthe*, Ger.)

The fruit, peeled, dried, and freed from seeds, of the *Citrullus Colocynthis* (Schrader), a climbing plant of the gourd family, inhabiting the warm dry districts of the Old World—India, Persia, Arabia, Syria, and the African and European shores of the Mediterranean. (*Cf.* Bentl. a. Trim. 114.)

Colocynth was well known to Greek, Roman, and Arabian medicine, and in the form of solid extract enters into many of the purgative pills of modern pharmacy. It was chemically examined early in the last century, amongst others by Braconnot (Journ. de Phys. 84, 338); Vauquelin (J. Pharm. Chim. 10, 416); Herberger (Rep. Pharm. 35, 368); Bostick (Pharm. J. 10, 289); and Meissner (Pereira, Mat. Med. 3rd ed. 2, 1737). It was, however, Walz, in 1858, who first isolated an active constituent, *colocynthin*, from the drug (Arch. Pharm. 96, 241; 99, 338; J. 1858, 531; 1861, 757). The alcoholic extract is treated with water, the aqueous solution precipitated by lead acetate and sub-acetate, and the clear liquid thus obtained, after being freed from lead by sulphuretted hydrogen, is precipitated by tannic acid. The precipitate dissolved in alcohol is freed from tannic acid by treatment with basic lead acetate, and the crude colocynthin thus obtained is finally purified by washing with ether. (*Cf.* Lebourdais, Ann. Chim. Phys. [3] 24, 58) and Henke Arch. Pharm. 221, 200.)

Colocynthin is a sticky mass, brittle when dry (Henke), is indistinctly crystalline (Walz). It has an intensely bitter taste, and acts as a drastic purgative. Walz assigns to it the formula $C_{56}H_{84}O_{23}$. Water and alcohol dissolve it, but it is insoluble in ether, chloroform, and most other solvents. Yield from the drug 0·6 p.c. (Henke). The aqueous extract reduces Fehling's solution. With concentrated acids, colocynthin gives colour reactions: with sulphuric acid, deep red; nitric acid, bright red; hydrochloric acid, bright yellow. According to Walz, colocynthin is a glucoside breaking up by treatment with dilute acids into glucose and a resinous product *colocynthein*. Johannson (Zeitsch. anal. Chem. 24, 154) also states that colocynthin, heated with dilute sulphuric acid, yields colocynthein together with elaterin and bryonin, and he describes colour reactions by which these products may be distinguished. Walz also obtained from the alcoholic extract of colocynth a crystalline substance, insoluble in water but soluble in ether, which he named *colocynthitin*.

Naylor and Chappel (Pharm. J. 79, 117) have prepared from the fruit of *Cucumis trigonus* (Roxb.) or pseudo-colocynth, a plant indigenous to India, a principle identical with or nearly related to colocynthin from *Citrullus Colocynthis*, and find that on hydrolysis it yields, amongst other products, colocynthein, elaterin, and dextrose. The same authors, by a modification of Henke's method, obtained colocynthin from *Citrullus Colocynthis* in a crystalline form.

Power and Moore (Chem. Soc. Trans. 97, 99) have cast doubt on the existence of the colocynthin and colocynthitin of previous investigators. In their research the pulp of the

fruit was examined separately from the seeds, and the following substances were isolated: *citrullol*, a dihydric alcohol $C_{22}H_{36}O_2(OH)_2$, m.p. 285°–290°, yielding a diacetyl derivative, melting at 167°; an amorphous alkaloidal substance possessing an extremely bitter taste and representing one of the purgative principles of the fruit; *a*-elaterin (*see* ELATERIUM); a small amount of hentriacontane $C_{31}H_{64}$, m.p. 68°; a phytosterol $C_{27}H_{46}O$; and a mixture of fatty acids. The seeds, which represent 75·5 p.c. of the peeled fruit, were found to contain traces of an alkaloidal principle, a small amount of an enzyme hydrolysing *β*-glucosides, and fatty oil. The proportion of glucosidal substance in the fruit is found to be very small. The purgative action depends on at least two compounds, one of which is alkaloidal. After removal of the alkaloidal compound, the fruit still possesses marked purgative properties, but the substance to which these are due has not yet been obtained in a definite form.

It has been sometimes required to search for colocynth in beer (*v.* Dragendorff, Chem. Zentr. 1881, 285, 299). A. S.

COLOGNE YELLOW *v.* CHROMIUM.

COLOPHON *v.* OLEO-RESINS.

COLOPHONY *v.* RESINS.

COLOPTENE *v.* RESINS.

COLORIMETERS, CHROMOMETERS, or CHROMATOMETERS. Under this heading are included those instruments (*colorimeters*) which are used for determining the relative intensity of colour in solutions, and those (*chromatometers, tintometers*) which are used to obtain a numerical record of the hue and intensity of a colour.

Colorimetric measurements depend on obtaining equal intensity of colour in two columns of liquid, one of which contains a known amount of the substance to be estimated. This can be done either (*a*) by varying the *concentration* of one liquid, keeping the lengths of columns equal, or (*b*) by altering the length of one column, keeping the concentration the same.

The first method is used in Nessler's test, in Eggertz' method of estimating carbon in steel, and in the simple colorimeter of the U.S. Geological Survey (Bulletin 422). It is applicable to all colorimetric measurements. The second principle is adopted in most cases because it allows the repeated use of the standard solution and facilitates rapid work. In certain cases, however, *e.g.* in comparing manganese solutions, this method fails, as varying the length of column changes the *hue* as well as the *intensity* of the colour.

The standard used may be of the same composition as the liquid under examination, or may be made of any suitable materials, but its colour must be identical in *quality* with that of the liquid tested, and its value per unit volume in terms of the substance estimated must be accurately known. Thus the permanent standards used in the estimation of combined carbon in steel are generally made of mixed solutions of *metallic salts*, and in the estimation of ammonia in water a solution coloured with *caramel* and a little *aniline red* has been used (Leeds, Chem. News, 37, 229).

Equality of tint having been obtained, the lengths of the columns are noted, and the comparison is repeated, using, preferably, a different length of column of the standard.

The relative strength of the solutions varies *inversely* as the lengths of the columns, so that if 1 c.c. of the standard solution correspond with x parts by weight of the substance estimated, the weight of that substance in 1 c.c. of the test solution will be

$$\frac{\text{length of column of standard solution} \times x}{\text{length of column of test solution}}$$

If the strength of the standard differ by more than 10 p.c. from that of the test liquid, it is advisable to dilute one or other before comparison.

For the examination of precipitates, a solution of considerable suspensory power is prepared by dissolving 100 grams of gelatine, 100 grams glacial acetic acid, and 1 gram of salicylic acid (to prevent decomposition of the gelatine by keeping) in 1 litre of distilled water.

The solution is clarified with white of egg and filtered hot. For estimation of sulphuric acid, this solution is charged with barium chloride, and is added to a weak standard solution of sulphuric acid or a sulphate and to the solution to be tested, the two turbid liquids being then compared as above. By the use of other reagents, lime, zinc, and a large number of other substances may be estimated.

A useful colorimeter for general purposes, devised by Mills, is shown in Fig. 1. It consists of a glass jar closed above by a cap of which the length is sufficient to cover the top of the liquid. The cap is perforated in the middle and carries a short tube in which slides a glass rod bent as shown, and supporting, exactly at right angles to the axis of the jar, a flat circular opaque white disc. In the bottom of the jar are laid, one above another, a red and a green glass disc which form a black background to the white disc. When examining solutions of certain colours, a background of a colour other than black may be advantageous, and the white disc itself may be covered by a coloured plate. The white disc is lowered to the bottom of the jar by moving its rod, and the jar is filled to exactly 100 divisions with a standard liquid.

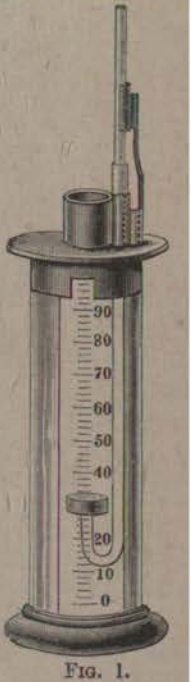


FIG. 1.

The white disc is raised until, on looking vertically down through the liquid at the disc, the depth of tint appears suitable. A second apparatus is then filled to 100 divisions with the liquid to be tested, and its disc is adjusted until the colours of the columns of liquid in the two jars appear of equal intensity.

By placing on the white disc a small, black, hemispherical button, this instrument may be used for determining the strength of turbid solutions, such as milk, or for ascertaining the

amount of a precipitate suspended in a liquid. Milk is diluted before examination with 99 parts of water, and is compared with a similarly diluted milk of known quality, the disc with the button being adjusted in each tube as above until just invisible.

The slight alteration in the level of the liquid caused by the varying length of the sliding tube contained in the liquid when adjusting the height of the white disc is found by experiment, and a correction must be introduced into the calculation for variations of more than two or three divisions.

A very useful colorimeter, especially designed for the estimation of carbon in steel, but of course available for other purposes, has been introduced by Stead (Proc. Iron and Steel Inst. 1883, No. 1, 213). A similar, but more convenient apparatus, devised by Ridsdale (J. Soc. Chem. Ind. 1886, 586) is shown in Fig. 2. Three glass tubes, each fitted below with a small,

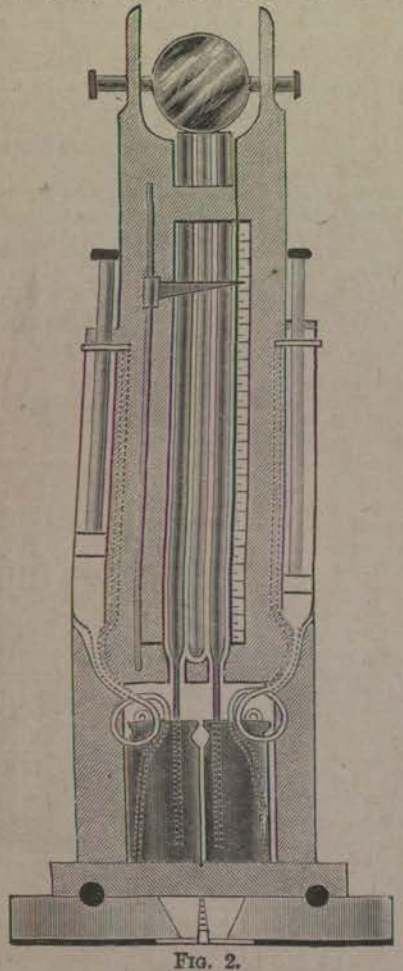


FIG. 2.

opaque, white cylinder, are placed beneath a movable mirror, in a stand which may be turned to any position upon its weighted base. The central tube is removable and is closed below; the outer tubes are drawn out and pass through indiarubber corks into ruby glass bottles, containing standard solutions of different strengths. Each bottle has a tube with a stopcock through which the liquid may be introduced or removed, and each is connected by a flexible tube with a syringe.

The liquid under examination is introduced into the central tube, and by working the syringes the standard solutions are raised in their tubes until the intensity of colour in each tube, as seen by looking into the mirror which is adjusted to reflect the light passing upwards through the tubes, is identical. Two distinct comparisons are thus simultaneously made, and, by noting the height of each column by means of the sliding pointer, the strength of the tested liquid may be ascertained from the formula already given. A very important advantage of this apparatus is that every part except the central tube is cleansed and recharged without disconnection.

Ridsdale (J. Soc. Chem. Ind. 1888, 70) has devised an apparatus for the examination of liquids of deeper tint than can be used in the foregoing apparatus. The central upper tube (Fig. 3) is sealed below, the upper side tubes are perforated at the bottom. Each tube contains a loose white opaque plug, and each is held at

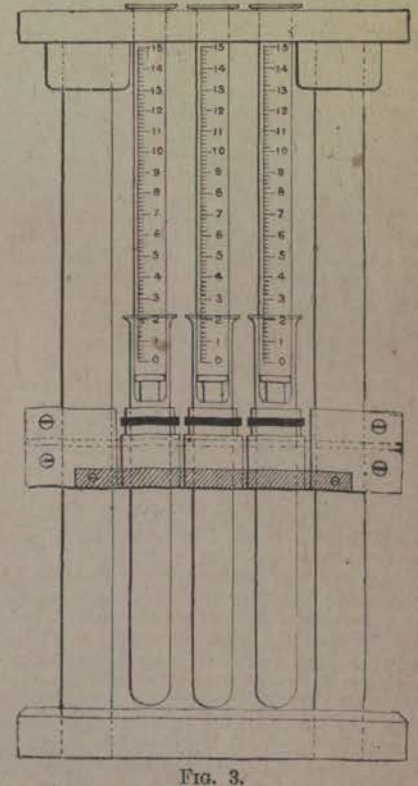


FIG. 3.

any height by a movable jaw pressed against it by an indiarubber band.

The centre tube is charged with, say, 10 divisions of the standard solution, and the test

liquid is run into one of the side tubes, whence it passes at once into the lower tube. When this is nearly filled, it is gradually raised to bring a portion of its contents into the upper tube, until, on looking down vertically, the colours in the upper side tube and in the standard tube are of equal intensity. The calculation is made as already described. The lower tube beneath the standard tube must be raised with that of the side tube in order to equalise the effect of the double thickness of glass. When the solutions to be tested differ widely in tint, the standard tube may be perforated so that the length of its column may be readily adjusted.

Stokes' apparatus (Chem. Soc. Proc. 1887, 135) has two tubes placed vertically in a stand with a reflector below. One tube is connected with a reservoir of the standard solution, by raising or lowering which the level of liquid in the tube can be altered.

A similar arrangement is used in Le Docte's colorimeter (Eng. Pat. 20667, 1898).

The Kennicott-Sargent colorimeter (Chem. Engineer, 1907, 213) differs from the above only in altering the level of the standard liquid by moving a glass plunger in a fixed cylindrical reservoir.

Another arrangement, in which the standard liquid is forced into a graduated tube from a reservoir, is described by Günsberg (Dingl. poly. J. 228, 457).

The Nesslerising tubes adopted by Hehner (Chem. News, 33, 185) and recommended by Milne (J. Soc. Chem. Ind. 1887, 33) are two cylinders of equal and perfectly uniform diameter, holding about 100 c.c. Each is graduated from below, and at about the 30 c.c. division has a glass stopcock.

The two cylinders are placed side by side on white paper, and to one of them is added 100 c.c. of the liquid to be tested, followed by 2 c.c. of Nessler's solution. To the other tube a suitable and known amount of standard solution of ammonium chloride is added, and the volume is made up to 100 c.c. with distilled water, after which 2 c.c. of Nessler's solution is added. The two liquids are looked at *vertically*, and the darker is allowed to slowly run off into a clean beaker, until their colours are equal. The comparison may be repeated after filling up from the beaker. The mode of calculation is the same as in former cases.

A modified form of Eggertz tube has been described by Hogg (J. Soc. Chem. Ind. 1895, 1022).

In a colorimeter devised by Leeds (Chem. News, 37, 229) comparison tubes are arranged in a rack, light being reflected through them by an inclined upper mirror, and again reflected to the eye of the observer from a mirror similarly placed beneath them. The standard liquid is contained in a bottle prism which is moved beneath one of the comparison tubes containing distilled water only until the colour observed is identical with that in the tube containing the test liquid. The strength of the test liquid is calculated from the thickness of liquid in that section of the prism which is interposed.

Gallenkamp's colorimeter (Chem. Zeit. Rep. 1891, 324) consists of two vertical troughs enclosed in a metal frame. That which contains the standard solution is wedge-shaped, while that for the test liquid is rectangular. An observation apparatus, moving vertically over a scale of 100 parts, has two slits at the same level, one opposite each trough, the light from which is reflected and brought into one eyepiece. The observation consists in finding the thickness of the stratum of standard solution in the prism, which shows the same depth of colour as the test liquid.

White's apparatus differs from the above in having two wedge-shaped tanks, both movable with reference to two fixed slits through which the depth of colour is observed.

A colorimeter, described by Autenrieth and Koenigsberger (Chem. Zentr. 1910, i. 2032) and recommended especially for the determination of hæmatine in blood, depends on comparison of the test liquid with a stable solution of similar hue contained in a wedge-shaped reservoir which is movable vertically beside the trough containing the test liquid. The movement of the wedge is measured on a millimetre scale, and the reading translated directly into percentages by reference to a plotted curve. The two colours are observed through a Helmholtz 'Doppelplatte,' which obviates a dividing space in the field of view. By substituting a suitable wedge, the instrument can also be used for the estimation of titanium, iron, chromium, iodine, ammonia, nitric acid, &c.

Schreiner's colorimeter (J. Amer. Chem. Soc. 1905, 1192) consists essentially of two parts: a wide flat-ended tube, B, about 26 cm. × 3 cm., graduated in millimetres, and the flat-ended immersion tube A, about 26 cm. × 2 cm., which slides inside the wider tube.

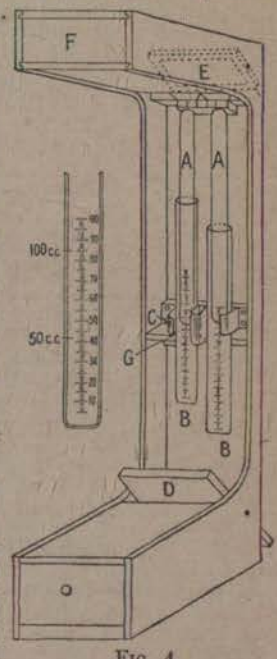


FIG. 4.

Two such pairs of tubes are mounted on a stand (Fig. 4), the inner tubes being fixed to the top of the camera while the outer tubes are held in brass clips which keep them in position, but permit their being moved up and down. The length of the column of liquid enclosed between the ends of the outer and inner tubes can thus be adjusted at will. Light, reflected from a white surface D, passes through the two columns of liquid, and is then reflected at a mirror E to the observer's eyes at F. The axes of the tubes are inclined to one another so as to bring the images close together. Standard glass slides may be inserted at G

in place of one of the wide tubes, the immersion tube being left in position.

Patterson has described (J. Soc. Chem. Ind. 1890, 36) a more complex apparatus employing the same principle. In this case the adjustment of the concentric tubes is made by rack and pinion, and total reflection prisms are employed to bring the two images into one eyepiece. By substituting a direct-vision spectroscope for the eyepiece, the apparatus becomes a *spectrum absorptimeter*.

The simple and effective colorimeter devised by Steiger (J. Amer. Chem. Soc. 1908, 215) consists of two wooden boxes painted dead-black inside, one of which (Fig. 5A) is mounted on a

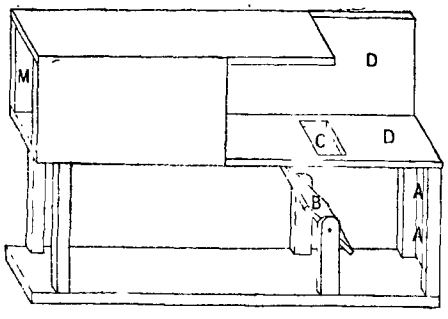


FIG. 5A.

stand and has a rectangular opening C in the base, while the second box (Fig. 5B) fits into the

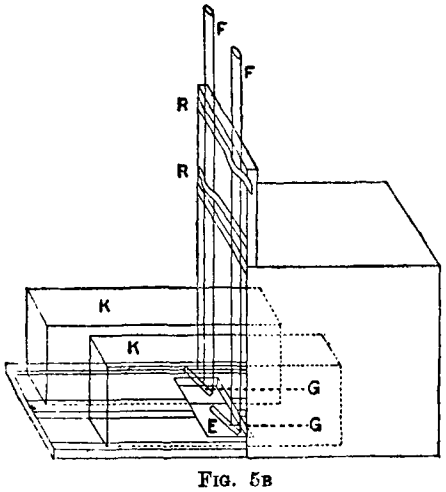


FIG. 5B

first, and has a rectangular opening E, which coincides with C.

In the base of this box are two grooves in which slide two rectangular glass cells K, K, about 15 cm. long × 2·5 cm. wide × 5 cm. deep.

Fixed vertically over the opening E are two glass rods F, F, held in place by the springs R, each carrying at the lower end a small plane mirror, G, fixed at angle of 45°. Light coming through the ground-glass A is reflected by a mirror, B, through the aperture E into the tank, where it is again reflected at the mirror G and passes through a column of liquid, the length of which can be altered by moving the tank backwards and forwards. When equality of colour is obtained, the lengths of the columns are read off on millimetre scales engraved on the base of each tank. The reading is taken where the lower edge of the mirror touches the bottom of the tank.

Otto's *ozonometer* has two parallel tubes for gases or liquids, and employs wedges of coloured glass moving over a graduated scale as a means of measuring the depth of tint (Eng. Pat. 17524, 1898).

H. Krüss suggests (Zeitsch. anorg. Chem. 5, 325) the application to colorimeters of the Lummer-Brodhun double prism, which gives a field of view in which there is no visible line of separation between the two colours under observation. This condition gives maximum accuracy in matching the colours (*see also* Chem. Soc. Abstr. 1894, ii. 158).

Andrieux (Compt. rend. 103, 281) describes an apparatus in which the *quality* and *intensity* of a colour are determined by comparison with a ray of polarised light.

An apparatus has been described by Meisling (Zeitsch. anal. Chem. 1904, 137), in which the hue is matched by the colour of a quartz plate in polarised light, and the intensity is measured by varying the length of the column of liquid.

An ingenious instrument, introduced by Mr. J. W. Lovibond, for the examination of liquids, powders, fabrics, &c., and known as the *tintometer*, is shown, partly in section, in Fig. 6. It consists of a box, closed at one end by a ground-

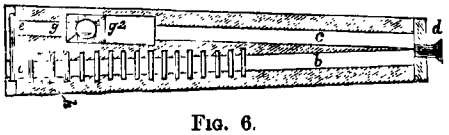


FIG. 6.

glass plate, *e*, and separated into two divisions *b*, *c*. The box is carried by a stand, adjustable to any angle. A square glass cell, of known width, along the line $g'g^2$, containing the solution to be examined, is placed in one division, and glass plates *h* of similar colour (or, if necessary, of different colours, producing the proper tint in combination), and of known intensity, are placed in grooves in the other division, until, on looking through both tubes simultaneously through a single eyepiece, *d*, shaded to prevent access of side light to the eye, the appearance through the glass plates is identical with that through the solution.

The standard plates are specially prepared of various colours, and each is distinguished by a number indicating its *colour*, and another number showing the *intensity* of colour, *i.e.* the number of plates of that colour of unit intensity required to produce an intensity equal to that of the plate. The unit chosen by the inventor for each colour is an arbitrary one, but its actual value can be ascertained at any time by comparison with a standard solution of similar colour.

In some cases the glass plate *e* is wanting, and an adjustable plane glass mirror is used to reflect the light to the apparatus (Eng. Pat. 12867, 1886).

When the colour of a fabric is to be estimated, the fabric is stretched on a block placed in the

division *c*, and a white fabric of *similar texture*, previously compared with a plate of pure *plaster of Paris*, is placed in the division *b*. The standard plates are then inserted as above until the appearances through the eyepiece are identical. *Powders, sugars, &c.*, pressed in a small tray placed in the division *c*, may be similarly examined, a tray containing pure plaster of Paris being placed in the division *b* (J. Soc. Chem. Ind. 1888, 234).

For very delicate observations, the intensity of the light used may be found and noted, before commencing, by closing the division *c* and placing in the divisions *b* as many standard plates of *neutral tint* as serve to obstruct all the light.

The substitution of a movable wedge of coloured glass for the standard plates makes the apparatus available for ordinary colorimetric determinations (J. Soc. Chem. Ind. 1888, 234). An improved form of Lovibond's apparatus is binocular, and has a movable diaphragm. This makes it applicable to tests of colour vision (*ibid.* 1891, 489) (*see also* Lovibond, *ibid.* 1909, 500).

Procter has described (*ibid.* 1895, 123) a modified form of tintometer in which, by a system of mirrors, the colours to be compared are brought close together in the field of view, thus giving greater accuracy.

Sczepanik (Eng. Pat. 22995, 1907) has patented an ingenious apparatus with which a numerical record of any colour can be obtained. Three strata of liquid of the three primary colours are superimposed. The thickness of each stratum can be measured and altered independently of the others, and thus any hue or intensity of colour can be matched.

Gardner and Dufton have introduced the 'Dalite' lamp, which gives a light of the quality of daylight, and may be used for tintometric work (J. Soc. Chem. Ind. 1904, 598). This lamp is also of use in performing titrations by artificial light.

A useful device, introduced by Dupré (Analyst, 5, 123), may be mentioned under this heading. In the volumetric estimation of silver with potassium chromate as an indicator, especially when the solution is weak, it is somewhat difficult, on account of the original yellow colour of the solution, to observe the first tinge of red produced by the formation of the silver chromate. Dupré interposes, between the eye and the test liquid, a flat glass cell (of which the faces are about half an inch apart) containing a solution of potassium chromate of such strength as will neutralise the colour of the test liquid, which thus appears perfectly colourless, and in which the faintest appearance of red is readily visible. The cell filled with other liquid may be similarly adopted in many other titrations.

König (Proc. Amer. Phil. Soc. [18] 7, 29, 184, 208, 211) has devised a method for estimating metals by the intensity of the colour imparted by them to the borax bead. He dissolves a known weight of the oxide in a known weight of borax, grinds the bead until its faces are flat, coats it with Canada balsam to render its rough faces transparent, and places it in an apparatus where it is viewed by a lens of small power, while, by means of a rack, a glass prism whose colour is complementary to that under examination, is moved before it until such a thickness is interposed that the colour of the bead is extinguished.

A photochemical process for estimating differences in the intensity of a colour has been described by E. J. Mills and Buchanan (J. Soc. Chem. Ind. 1888, 309). It has been applied to the comparison of dyed goods. A number of discs of the tissues are photographed on one negative from which a number of positives on paper sensitised with silver, are copied. These are treated as usual, soaked for a considerable time in sodium thiosulphate to remove the whole of the unaltered silver salt, well washed, and dried. The disc photographs of each tissue are cut from a number of positives and each set is burned separately. The silver in the residue is dissolved and estimated volumetrically. The relative amount of silver found in the different sets of discs directly represents the relative intensity of the colours.

The following colorimetric process for the estimation of minute quantities of sulphur in iron, mineral waters, black ash, slag, &c., is due to Wiborgh (Chem. Zeit. 10, 92; Chem. News, 1886, 54, 158).

The divided metal, ore, &c., or the concentrated solution, is introduced into a small flask provided with an indiarubber cork, through which passes a stoppered funnel for introduction of acid, and a narrow-mouthed funnel ground at the top. A disc of white calico, which has been previously saturated with a solution of 5 grams crystallised *cadmium nitrate* (or, preferably, *cadmium acetate*) in 100 c.c. of water and dried in a horizontal position on a cloth, is fixed between two indiarubber rings of the same interior diameters as the standard discs hereafter described, and the rings are firmly clamped over the funnel mouth. Dilute sulphuric acid is poured into the flask and heat is applied. In from 30 to 45 minutes the whole of the sulphur which is capable of conversion into sulphuretted hydrogen has passed off in that form and has been *wholly* absorbed by the cadmium salt on the calico. The disc is removed and compared with a set of standard discs, similarly prepared from iron containing a known amount of sulphur. The standard discs should not be exposed too freely to light. Arsenic, carbon silicon, and copper do not appear to affect the determination. This method is so delicate that a disc will show a t nge of the yellow colour due to the cadmium sulphide when so small a quantity as the 1000th of a milligram of sulphur is present per square centimetre.

COLUMBA or **COLUMBO; COLUMBIC ACID** and **COLUMBIN** *v.* CALUMBA.

COLUMBIA BLACK, -BLUE, -GREEN *v.* AZO- COLOURING MATTERS.

COLUMBIA YELLOW *v.* PRIMULINE AND ITS DERIVATIVES.

COLUMBITE. A columbate (niobate) of iron, usually containing some manganese and tantalum, the general formula being

$$(Fe,Mn)(Cb,Ta)_2O_6.$$

With an increase in the amount of tantalum, there is a transition to the isomorphous species, *tantalite* (*q.v.*). The orthorhombic crystals are dark brown or black and opaque, and range in sp.gr. from 5·3 (columbite) to 7·3 (tantalite). It was in this mineral that C. Hatchett discovered, in 1802, the element columbium, so

named because the specimen he examined came from America. Columbite is found as single crystals embedded in pegmatite at Haddam in Connecticut, Chesterfield in Massachusetts, Moss in Norway, &c. L. J. S.

COLUMBIUM (*Niobium*). Sym. Cb. At. wt. 93·1 (Smith and V. Haagen). Although this metal is still commonly termed niobium by the mineralogist and the metallurgist, the name columbium, which was given to it in 1802 by Hatchett, who first isolated it in the form of a new 'earth' (Cb_2O_5) from a mineral found in Connecticut, has been officially adopted by the chemist in English-speaking countries, and generally throughout the world, except perhaps, in Germany.

Columbium is a member of a group of comparatively rare metals, including tantalum, tungsten, molybdenum, titanium, and uranium, commonly occurring together in minerals found in the oldest Plutonic rocks and especially in and around intrusions which traverse pegmatites and other extremely coarse-grained granite rocks. Monazite, and other minerals containing metals of the cerium group, zircons, cryolite, and fluorspar, and minerals containing lithium, cæsium, and rubidium, are often associated with these minerals, and are probably intimately connected with their genesis.

Although an extremely rare metal, columbium exists as the pentoxide in a considerable number of minerals, in some of which—such as pyrochlore and columbite—it may be regarded as the essential constituent, while, in others, although practically always present, its proportion varies from a mere trace up to an amount which justifies its being considered as the principal oxide.

Columbium occurs in minerals only as the pentoxide Cb_2O_5, in combination with a base, the columbium in the few minerals (such as wöhlerite) which contain silica, being present as a silico-columbate, and never as a silicate of columbium.

A list of thirty or forty minerals in which columbium is commonly found in association with tantalum might be given, but the principal will be given in the article TANTALUM, with which metal columbium invariably occurs in nature. From the technical point of view, the principal columbium minerals are those which consist essentially of columbates of iron, manganese, and lime, zirconia and metals of the cerium group being also usually present in, or at any rate intimately associated with, such minerals as contain lime.

The mineral richest in columbium is *pyrochlore*, a columbate of lime containing titanium, cerium, and thorium, together with other alkaline earths and alkali bases and some fluorine. The most important mineral, however, is the columbate of iron and manganese known as *columbite* or *niobite*, in which the Cb_2O_5 may even exceed 78 p.c., a condition nearly reached by certain specimens occurring in the cryolite of Arsukfiord (Greenland).

The columbium is always partly replaced by tantalum, the proportion of which may vary from a trace through all gradations, until the mineral merges into tantalite which is isomorphous with columbite, and which occurs in much larger quantity and furnishes the bulk of the tantalum of commerce and, as a by-product, of the columbium. These two minerals are found in alluvial deposits with cassiterite and wolfram, and in isolated masses left by the denudation of intrusions in pegmatites, &c., at Greenbushes and elsewhere in Western Australia, in Colorado (Cañon City), Dakota (Black Hills), North Carolina and other districts of the United States, and in Sweden, Norway, Greenland, and many other districts. They may be considered to possess the general formula $(FeMn)O(CbTa)_2O_5$, the relative proportions of ferrous and manganous oxides varying within extremely wide limits.

New deposits are constantly being discovered, and columbium, like many others of the rare metals for which a demand now exists, will doubtless be found to occur in much larger quantities than is generally believed.

Amounts, far in excess of present requirements, are obtainable as by-products from the preparation of the rare earths employed for incandescent mantles, from tin and wolfram ores, and from the heavy waste material obtained in the dressing of cryolite.

Metallic columbium may be prepared by passing a mixture of the vapour of the pentachloride and hydrogen through a red-hot tube (Roscoe); in a less pure condition, by heating the pentoxide with carbon in the electric furnace (Moissan); by the alumino-thermic process, and by the method of von Bolton, introduced with a view to the manufacture of metal filament lamps, before tantalum came into use. In this process, the pentoxide is mixed with paraffin and formed into threads which are heated *in vacuó* to a temperature of over 1900° by passage of an electric current.

By the alumino-thermic reaction, von Bolton has obtained columbium containing about 3 p.c. of aluminium which can be driven off with other impurities by prolonged heating *in vacuó* in the electric furnace. The purest columbium hitherto prepared in bulk is said to have been thus obtained. Like tantalum, it can also be obtained by reduction of the fluoride K_2CbF_7 with potassium, as a black powder from which the residual hydrogen may be expelled by shaping it into small cylinders and melting *in vacuó* in an electric furnace.

Although the most important use of tantalum is for manufacture of electric lamps, in which case it requires to be separated from columbium, the amount actually consumed for the purpose is extremely small. The standard tantalum lamp, introduced in 1904, contained only one twenty-thousandth of a pound of tantalum, and those now manufactured contain much less.

The method employed for the separation of columbium from tantalum in the preparation of the latter element for electric lamp filaments probably depends essentially upon a fractional crystallisation of the mixed double fluorides of potassium with tantalum, columbium, and titanium.

There is reason to think that the peculiar virtues imparted to steel by tantalum, in common with tungsten, molybdenum, vanadium, uranium, and zirconium, will result in a larger demand for tantalum, and this property is shared by columbium. The ferro-tantalum at present

manufactured for this purpose is prepared from tantalite containing columbium by direct smelting in the electric furnace, and contains much of the latter metal, no attempt being made to separate it.

Similarly, should the suggested use of tantalum in place of steel for surgical, dental, and other purposes, or in the manufacture of acid- and alkali-resisting utensils, be found practicable, it is possible that the alloy prepared from the mixed tantalic and columbic acids obtained from minerals containing both, may be as suitable as either metal alone.

Metallic columbium melts at 1950°, and has a sp.gr. of 12·7, and an electrical resistance of 0·1870 ohm for a wire 1 metre long by 1 mm. diameter. It is less malleable or ductile than tantalum, but the rolled metal has a hardness greater than that of wrought iron, and may be welded at a red heat.

Although the powdered metal oxidises rapidly when heated in air, the rolled or cast metal is but little affected, as a protective coating of oxide rapidly forms. It is practically unaffected by any acid except hydrofluoric acid, or by solution of the alkalis, but is rapidly attacked by fused alkalis or alkaline nitrates.

It combines with carbon when heated, and at dull redness rapidly absorbs hydrogen or nitrogen and becomes brittle, the hydride and nitride respectively being apparently formed.

It reacts violently when heated with sulphur or selenium, and forms the volatile pentachloride when heated to redness in chlorine.

It does not form an amalgam with mercury, but alloys with many other metals and in all proportions with iron.

The compounds of columbium have not yet been applied commercially, but the pentoxide, generally known as columbic acid, and the fluorides, especially the double fluoride with potassium $2KF{\cdot}CbF_5$ are of interest in connection with the preparation of the pure compounds or metal from minerals. G. T. H.

COLZA OIL *v.* RAPE OIL.

COMENAMINIC ACID *v.* BONE OIL.

COMMON CAMPHOR *v.* CAMPHORS.

CONCRETE *v.* CEMENT.

CONDENSERS. A condenser is an apparatus in which the vapour of a liquid may be cooled down to a temperature below that at which it is converted into the liquid state under the prevailing pressure. The condensation of the vapour is usually effected by bringing it into contact with a cold surface, to which it imparts its heat, suitable arrangement being made for conveying away this heat from the cooling surface. Although air cooling is sometimes depended upon for this latter purpose, the arrangement usually adopted consists in causing a stream of cold liquid (water in the majority of cases) to circulate over the exterior of the condensing chamber. The following points should be considered in the designing of an efficient condenser:—

(*a*) The cooling surface must be made of material upon which the vapour has no chemical action, and should be capable of withstanding repeated variations of temperature without fracture.

(*b*) The area of cooling surface should be as great as possible, without making the apparatus unduly large and heavy.

(*c*) The material should preferably have a high specific heat, so that its rise in temperature may be kept within reasonable limits; and it should have a high thermal conductivity, in order that the heat it absorbs may be rapidly carried away.

(*d*) The design should be such as to admit of the condenser being readily cleansed.

It is not possible to obtain materials entirely satisfactory in each of the above respects, and so in practice the materials employed are those which combine cheapness with reasonable satisfaction in the foregoing particulars. For laboratory apparatus, the material commonly used is glass; metals (block tin, copper, &c.) are less often employed, except for constructing fairly large pieces of apparatus; of recent years, silica has found a limited use.

Condensers are used in two different kinds of operations: (1) for condensing vapours in distillation processes, in which case a still is attached to the upper end and a suitable receiver to the lower end; and (2) as 'reflux' apparatus in cases where it is necessary to boil a liquid for some time without sensible loss through evaporation; the vessel containing the boiling liquid is then attached to the lower end of the condenser and the condensed vapours flow back into the vessel. A number of condensers described below are specially designed for this purpose.

The simplest type of condenser is the familiar form devised by Weigel in 1771, but usually known as Liebig's condenser. It consists simply of a straight cylindrical glass tube, in which the vapour is condensed. The upper end is widened out slightly to facilitate connection with the still, and its lower end is cut off obliquely; a cylindrical glass jacket is slipped over the greater portion of the length of the tube, and through it, by appropriate entrance and exit tubes, cold water is circulated in an upward direction, so that the vapours passing down the inner condenser tube encounter a surface the temperature of which continuously falls in the direction of the receiver. This type of condenser admits of considerable variation and modification in the precise details of construction; thus, with a view to exposing a large cooling surface, the portion of the condenser within the jacket is sometimes made of approximately rectangular section, thus ⬭, being broadened considerably in one direction; in other condensers the central portion carries a series of bulbs blown on it. Cooling surface is obtained in some condensers by replacing the central portion by a closely wound glass spiral, as in Fig. 1, the water-jacket being sealed on to the condenser proper. The modified Liebig condenser, shown in Fig. 2 (Chem. Zeit. 1902, 26, 633) is arranged for use with the two limbs *a* and *c* of the inner U-tube on the same level to prevent accumulation of liquid at *b*. The inner tube is fused into the outer tube at *d*.

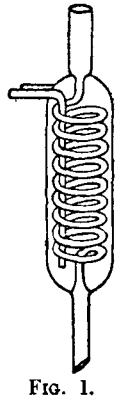


FIG. 1.

Glass condensers with water-jackets sealed on are restricted in their use to the condensation of the vapours of liquids of fairly low boiling-point (below 100°), since otherwise the glass

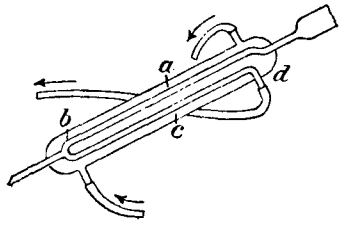


FIG. 2.

joints are liable to crack. For liquids of moderately high boiling-point (140°–200°), it usually suffices to employ merely the inner tube of a Liebig condenser (air condenser).

In the reflux condensers illustrated in Figs. 3 and 4 (J. Soc. Chem. Ind. 1897, 16, 979) the relative positions of the vapour and cooling stream of water are reversed, the water entering as shown by the arrows (at *a* in Fig. 3). A large area of exposed surface is obtained in these condensers, which, it will be observed, are of the 'double-surface' type, since, in addition to the inner water-cooled surface, condensation also occurs on the outer surface, which exposes an even larger area to the cooling action of the air.

Several vertical condensers have been devised by Friedrichs in which one of the two surfaces between which the vapours condense is constructed spirally (Zeitsch. angew. Chem. 1910, 23, 2425).

A number of extremely useful, compact condensers of the 'double-surface' type have been

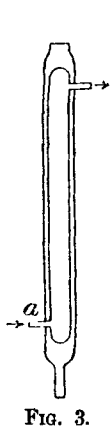


FIG. 3.

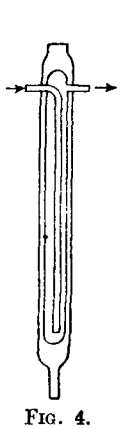


FIG. 4.

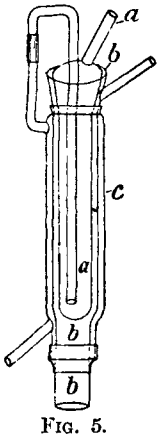


FIG. 5.

described. The vapours are condensed in the annular space between two surfaces, both of which are water-cooled, the design being such that one stream of water flows in succession over each. The efficiency of this cooling process is so great that these condensers can be made quite short; they are readily fixed in a vertical position and occupy little bench space.

In the Burgess condenser (J. Soc. Chem. Ind. 1905, 24, 1190), the tubes *a* and *c* (Fig. 5) are the cooling jackets, and *b* is the condensing tube proper. Cribb's condenser (Fig. 6) consists of two concentric tubes joined together at the top; condensation is effected in the interior chamber thus formed. Water is conveyed into the inner tube by the tube *a*; overflowing, it passes round the exterior of the outer tube and flows away by the side tube *b*. The vapour is led in through the inlet tube *c*.

Another double-surface condenser of simple construction is illustrated in ANALYSIS (Vol. I. p. 209).

The condensers illustrated in Figs. 7 and 8

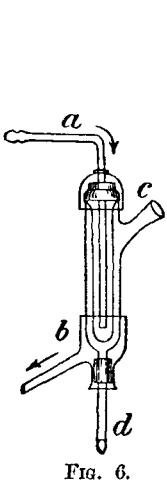


FIG. 6.

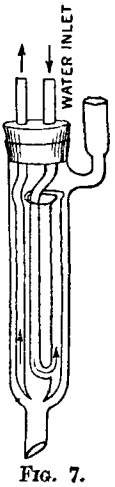


FIG. 7.

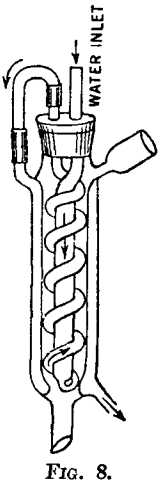


FIG. 8.

have the advantage of exposing four cooling surfaces to the vapour, and may be readily cleansed when necessary by removing the inner portions with the stopper (Chem. Zentr. 1908, ii. 277).

The condensers so far described are usually constructed of glass, but occasionally metals are employed. The use of *aluminium* for the inner tube of a Liebig condenser has been advocated by Norton (J. Amer. Chem. Soc. 1897, 19, 153). Many agricultural chemists, who have to deal with numerous ammonia distillations, prefer block-tin condensers; they are constructed like inverted U-tubes, one arm (the condenser arm) being much longer than the other and carrying a water-jacket if required, while the short arm is attached to the distilling flask. A convenient method of constructing a number of such condensers in series to be cooled by one stream of water is described in J. Amer. Chem. Soc. 1906, 28, 999.

A useful metallic condenser is the 'ball' type, used on the reflux principle in numerous experiments involving extractions with volatile solvents. Soxhlet's pattern is shown in Fig. 10, while the construction of a double-surface condenser of this pattern is sufficiently indicated in Fig. 9. Storch's metallic reflux condenser is depicted and described in J. Soc. Chem. Ind. 1897, 16, 979.

The spiral (worm) type of condenser is frequently constructed of metal (copper) and enclosed in a metal tank which can be filled with cold water; these condensers find considerable use in small plants for preparing distilled water. For this latter purpose, a novel

form of condenser is described in Eng. Pat. 6916, 1905, which combines efficiency with extreme simplicity of construction. The condenser, which is placed vertically above the evaporating chamber, consists of two metallic truncated cones, the lower being open at the top, while the upper is closed by a dome-shaped

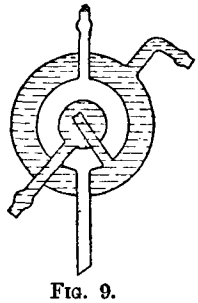


FIG. 9.

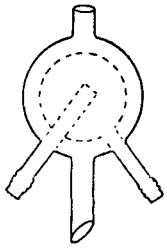


FIG. 10.

lid. The outer surface of the upper cone is cooled by a continuous stream of cold water, and condensation is effected upon its inner surface. The condensed vapour collects in the annular space between the two cones, and the water is continuously run off into large earthenware jars. Special apparatus, devised for preparing pure distilled water (so-called 'conductivity water') on a laboratory scale are described by Bousfield (Chem. Soc. Trans. 1905, 87, 740); Golding (J. Soc. Chem. Ind. 1906, 25, 678), and by Hartley, Campbell, and Poole (Chem. Soc. Trans. 1908, 93, 428).

Condensers of various designs are described in J. pr. Chem. [2] 34, 427; [2] 49, 44; Compt. rend. 118, 478; Ber. 1892, 24, 3950; 1895, 28, 2388; J. Soc. Chem. Ind. 1899, 18, 707; Chem. Zeit. 1902, 26, 325; 1904, 28, 598, 686; 1905, 29, 809; 1910, 34, 116; Bull. Soc. chim. 1904, 31, 1116; Chem. Zentr. 1906, ii. 993; and reflux condensers in Chem. Zeit. 1896, 20, 462; 1904, 28, 598; Bull. Soc. chim. 1901, 25, 476; 1908, 3, 855; Zeitsch. anal. Chem. 1901, 40, 769; Chem. Zentr. 1906, ii. 993; Chem. News, 1907, 95, 52; and J. Soc. Chem. Ind. 1908, 27, 962.

CONDURANGO. The dried bark of *Marsdenia condurango* (Nichols) (*Gonolobus Condurango triana*, Reichenbach; family *Asclepiadaceæ*). It is obtained from a half-climbing or prostrate shrub of Ecuador. The bark comes into commerce in quills or quilled pieces, about 10 cm. long, and rarely exceeding 2 cm. in diameter; externally brown grey, roughened, with scale like warts; internally, greyish or pale brownish-white, striate; fracture short, granular or slightly fibrous in inner layer. Taste, somewhat bitter; odour of fresh bark, aromatic.

Kubler (Arch. Pharm. 1908, 246, 620) states that the principal constituents of the bark are dextrose, other usual components of plants, the glucoside *condurangin* and a polyhydric alcohol *conduritol*. *Condurangin* $C_{40}H_{60}O_{16}$ contains two methoxyl groups, is soluble in water, alcohol, and chloroform, insoluble in ether. Dilute sulphuric acid hydrolyses it to dextrose and an amorphous powder, containing several substances; alcoholic potash yields some cinnamic acid. *Conduritol* $C_6H_{10}O_4$ crystallises from hot alcohol in colourless prisms, and yields a tribenzoyl derivative, m.p. 142°–143°. According to Carrara (Gazz. chim. ital. 21, i. 204; 22, i. 236), commercial condurangin can be separated into two parts, one insoluble and the other soluble in water. The former is a white powder, $C_{20}H_{32}O_6$, m.p. 60°–61°; and the latter a yellow substance, $C_{18}H_{28}O_7$, m.p. 134°. Hager (Handbook, 1900) has further investigated these substances and named them *a*- and *b*-condurangin; *a*-condurangin gives a green colour with Froehde's reagent (conc. sulphuric acid and molybdic acid), *b*-condurangin does not. Carrara (*l.c.*) also isolated a yellow powder, $C_{30}H_{50}O_2$, which he named *condurasterin*, m.p. 52°. Flückiger has isolated a small quantity of an alkaloid having a strychnine-like action. Firbas (Pharm. J. 70, 417) treats the chloroform extract of the crude glucoside with a mixture of equal volumes of sulphuric acid, hydrochloric acid, and alcohol (Lafon's reaction). On warming, a green colour is produced, changing to bluish-green on the addition of a trace of ferric chloride. Certain other glucosides give this reaction, but they are not likely to be present in the bark.

Condurango has been employed for many years in South America as an alterative in the treatment of syphilis. It is used as a stomachic, and lessens gastric catarrh and relieves the vomiting and nausea which are usually associated with carcinoma of the stomach; it is also used to lessen the pain consequent upon gastric ailments. Condurango produces in large amounts incoördination of the muscles and convulsions, which may be followed by paralysis. Dose, 1 fluid drachm of the fluid extract of condurango, or 4 fluid drachms of the wine of condurango.

There are many other varieties of condurango and marodenias. The Guayaquil condurango has several peculiarities in the wood of the bark, and has not so many medullary rays. Mexican condurangos contain a strong collenchyma next to the bark, while nearer the pith is a layer of bast fibres containing large crystals of calcium oxalate (Chem. Zeit. 11, 1601; 12, 26).

CONDY'S FLUID *v.* MANGANESE.

CONESSINE *v.* VEGETO-ALKALOIDS.

CONGO BLUE, -BROWNS, -CORINTH, -FAST BLUE, -ORANGE, -REDS, -RUBINE, -SKY BLUE *v.* AZO- COLOURING MATTERS.

CONIFERIN *v.* GLUCOSIDES.

CONIINE, CONICEINE *v.* VEGETO-ALKALOIDS.

CONIMA RESIN, CONIMENE *v.* OLEO-RESINS.

CONQUINAMINE *v.* VEGETO-ALKALOIDS.

CONVOLVULIN *v.* GLUCOSIDES.

COOMASSIE NAVY BLUE, -WOOL BLACKS, *v.* AZO- COLOURING MATTERS.

COPAIBA BALSAM *v.* OLEO-RESINS.

COPAIBA OIL *v.* OILS, ESSENTIAL.

COPAIVENE, COPAIVI, COPAIVIC ACID *v.* OLEO-RESINS.

COPAL *v.* RESINS.

COPAL VARNISH *v.* VARNISH.

COPALIN *v.* RESINS.

COPPER. Sym. Cu. At. wt. 63·57. Melting-point in air, 1062°; in reducing atmosphere, 1084°. Specific gravity: Roberts Austen (Int. Study of Met. 1902, 16) gives 8·217 as the sp. gr. of the molten metal. Copper, deposited by electrolysis from an acid solution of copper

sulphate and not subjected to any mechanical treatment, was found to have sp.gr. of 8·9544 at 15·5° in air (Watson, J. Soc. Chem. Ind. 2, 153).

Commercial copper, prepared in the usual way, is never pure, and the examination of the fractured surface of a cast ingot of copper shows a minutely vesicular structure. On this account the density of such metal is less than the same sample of metal after it has been subjected to a compressing mechanical treatment.

Colour.—Copper has a characteristic red colour which, in a fractured surface of worked metal, may be described as salmon-red. The only other metallic substance which at all resembles copper in colour is the titanium cyanonitride, which is sometimes formed in blast furnaces working on iron ores containing titanium.

Lustre.—A smooth cut or polished surface shows a bright metallic lustre which, however, soon tarnishes.

Crystalline system.—Copper crystallises in the cubical system.

Ores of copper. The following minerals are those from which copper is extracted on a commercial scale: native copper, cuprite, melaconite, malachite, azurite, chrysocolla, atacamite, chalcocite, bornite, chalcopyrite, fahl ore.

The importance of the several species in the above list as ores of copper varies very much with the locality. Thus, while native copper is the chief ore in the Lake Superior district of North America, and atacamite in one or two localities in Chile, they would in other localities, and generally, be looked upon as rather rare, especially so in the case of the last species mentioned. So also in the case of malachite; this species, as an ore of copper, is seldom met with except in small quantities in the upper and oxidised portions of some copper lodes; yet in the case of the once celebrated Burra Burra mine in Australia, and at Nischne-Tagilsk in Russia, it formed the bulk of the ore produced.

Generally, in a copper-mining district, all the oxidised species mentioned above occur in varying proportions, but as depth is attained, and almost invariably at or about the level at which water is reached, the copper-bearing minerals change and the oxidised species give place to the richer sulphide species, and these finally to chalcopyrite intimately mixed with varying proportions of pyrite. The intermingling of the two species last mentioned is frequently so intimate that it is not easy to distinguish the component minerals or to separate them. Chalcopyrite thus diluted down, as it were, with one or more of the minerals—pyrite, pyrotite, &c.—forms the ore from which the greater proportion of the world's copper supply is derived and the bulk of the material treated at the smelting works generally. Such ore frequently contains appreciable quantities of gold and silver and, almost universally, nickel, in quantities varying from traces upwards. The silver is frequently carried by intermixed fahl ore, but also, in many instances, by the pyritic mixture in which distinct silver-bearing minerals are not observable.

As by far the larger proportion of ore presented for metallurgical treatment is of the nature indicated above, viz. chalcopyrite mixed with varying quantities of the pyrite family of minerals, it will best serve the purpose of this article if the methods adopted for the extraction of copper from this material are considered, and in the following description of processes it is to be understood that ore of this character is referred to.

The elimination of the several elements in the ore and the final production of the copper in the metallic state, are effected by two distinct series of chemical operations. One of these—the most important, because of its very general application—treats the ore by smelting, and causes the necessary reactions to take place while the material is in a molten condition. The other—of very limited application—treats the material in the wet condition, and causes the necessary reactions to take place in solutions of the material.

These two distinctly different methods of procedure may be distinguished as (*a*) dry methods, and (*b*) wet methods.

Dry method. The object which the smelter keeps in view in the first stages of the process is to concentrate the copper contained in the ore in as small a quantity of material as may be economical. For this purpose, the product known as 'matte' or 'regulus' is universally selected. This is a combination of cuprous sulphide Cu_2S and iron sulphide FeS in varying proportions, together with sulphides of such other metallic elements as are capable of entering into the molten matte. The whole of the copper contained in the ore thus passes into the matte, while the silica combines with iron oxide and earthy bases, if present, and forms the slag. The slag, free from copper, separates easily from the matte, owing to its lower specific gravity, and is thrown away. Having thus concentrated the copper into regulus, or matte, the next stage of the process concerns itself with the decomposition of this matte in such manner as to eliminate the iron and sulphur and, as far as possible, other metallic elements which may be present and to yield the copper in the metallic state.

The final process consists in refining the copper produced as above; or, in other words, removing, as far as practicable, the small quantities of such elements as may still be present in the product of the preceding operation which would injuriously affect the copper for manufacturing purposes.

The treatment of the ore involves, therefore, three distinct operations:—

I. Smelting the ore with the production of matte and slag.

II. Treatment of the matte for the production of crude copper.

III. Refining.

The methods and the plant used for carrying out each of the three operations vary considerably, and the choice of any one depends upon local conditions, the nature of the ore as regards physical character, and the nature and quantity of the foreign elements present. It will not be possible within the limits of this article to study these considerations and the bearing they may have on the methods to be adopted; all that the space will allow of is a description of the methods as actually carried out under the most generally prevailing conditions.

I. *Smelting the ore with the production of matte and slag.*—The object of this process being the concentration of the copper in the matte, the chief considerations kept in view are the production of a matte as rich in copper, and a slag as poor in copper, as is practically and economically possible.

The grade of the matte to be produced having been decided upon, the smelter regulates this by suitably proportioning the sulphur in the ore to be treated so that there shall be sufficient to form Cu_2S with all the copper, and a further proportion to form FeS with the iron present in such quantity as will cause the matte to contain the desired percentage of copper. From these considerations it will be seen that the factor which regulates the grade of the matte is the quantity of sulphur present in the ore mixture smelted. With the class of ore under consideration, it invariably happens that the quantity of sulphur present is considerably in excess of requirements, and the production of the most suitable grade of matte necessitates the removal of this excess, which may be, and generally is, effected before the actual smelting of the ore is commenced. Under certain favourable conditions, however, it may be removed during the smelting process (*see Pyritic smelting*). This preliminary operation is designated 'calcining' or 'roasting,' the former term being more often used by English smelters and the latter by Americans. It is obvious that, as it is the total sulphur in the charge to be smelted which is concerned, either the whole of the ore may be taken and a small proportion of this element removed, or a small proportion of the ore may be taken and a large quantity of the sulphur removed. A suitable mixture of this latter with raw ore, so as to give the necessary total quantity of sulphur in the mixed charge, can then be used.

Whichever course is adopted, the mode of carrying out the operation is practically the same. The process consists in subjecting the ore to a dull red heat under oxidising conditions, so that the sulphur is caused to combine with oxygen derived from air admitted into contact with the ore with the production of sulphur dioxide, while the iron is also oxidised at the same time.

The method of carrying out this calcining process depends upon whether the ore is to be treated:

(*a*) In the rough—say in pieces from ¾ inch cube upwards; or

(*b*) Whether it is to be treated as fines or 'concentrates,' *i.e.* in which the particles are less than ¾ inch cube.

Under (*a*): *The ore may be calcined by forming heaps of it in the open air* and starting the combustion by means of a small proportion of wood, the combustion being maintained by the sulphur present in the ore.

The ore may also be calcined in stalls more or less open. These consist of series of chambers in rows built back to back. The chambers are each bounded by three walls, viz. back and two side walls, but are open in front and have no roofs. Small flues, opening out into the chambers, are built in the walls separating them, and these flues connect with a larger flue in the central division wall between the two rows, and these again connect with a chimney stack.

The ore is charged into these open chambers on to a layer of wood; when filled up, the wood is fired and combustion extends to the ore itself in the same way as in the case of the heaps. The gases produced in the operation are to a large extent led away by the flues in the walls above referred to. The annoyance caused by the escape of these gases at or near the ground level of the works—as is the case in open-heap roasting—is in this way to a large extent avoided.

The ore may be calcined in kilns.—These are similar to the stalls, but are generally built of much larger size, are closed in on all four sides, and are roofed over. They are provided with suitable openings in the roof through which the ore is introduced, and a doorway in the front wall (bricked up when the kiln is in operation) through which the calcined ore is removed. An outlet flue, connected to the roof or back wall, allows the gases to be conveyed to a chimney.

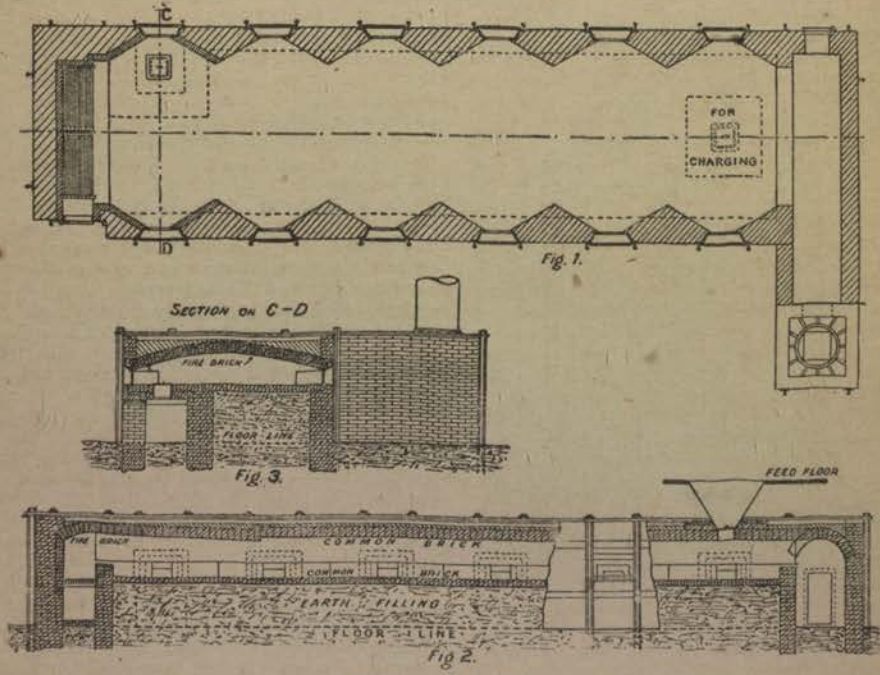
The ore may be calcined in 'burners.'—These are constructed and worked on very much the same lines as the 'burners' used for burning 'pyrites' at sulphuric acid works, and—in the case of copper ore—are the most suitable form of plant, if the gases evolved in the operation are to be used in the chamber process of making sulphuric acid. In this plant, a number of closed cells or 'burners' are built in rows, back to back. Each cell is roofed in and connects at the back with a central flue common to all the cells, by which the gases are led to the acid chambers. In the roof of each cell is an opening through which the ore can be charged from a hopper placed above. This opening is capable of being closed and is only open during charging. In this class of plant, the ore does not rest on the floor as it does in each of the cases previously considered, but upon a series of square bars suitably spaced. These bars are formed with circular necks where they are carried by the bearers, and can be rotated by applying a box key to their square ends. Below these bars is an enclosed space with suitable door through which the calcined ore is removed and by means of which the air supply is regulated.

In operating this plant, the cell having been brought up to a good red heat by the combustion of wood or other suitable fuel, ore in small quantities is gradually added as combustion proceeds, until the burner is full. At suitable intervals, a small quantity of the calcined ore is removed from the bottom of the burner and a corresponding fresh supply of ore is added through the opening in the roof. In this way, the operation of the burner is rendered continuous, and no fresh extraneous fuel is required after the first starting of the fire. The removal of the ore at the bottom of the burner is effected by rotating, or rocking, the square bars upon which the ore rests. As the space between the bars can in this way be made to vary from the distance between the bars when in this position , to the distance when in this position , the ore is caused to fall through in any quantity desired, and by this means, and by occasional working with long bars

through suitable holes provided for the purpose in the upper portion of the burner, the passage of the ore from top to bottom is facilitated.

In all the methods of treatment described under (*a*), it is essential that proper care be taken to prevent the temperature reaching anything like melting-point. If the ore melts or sinters together, calcination is delayed owing to the reduced surface on which oxidation can take place. Further, in the case of such sintered or melted material, difficulties are created in working the process. In the case of heap roasting and also in the stalls and kilns, the formation of large masses of sintered or melted ore introduces undesirable irregularities in the air current through the mass of ore under treatment, and causes trouble when the ore is removed. In the burners, the formation of sintered masses of ore must be avoided, as such masses would have to be broken up in the burner with suitable tools before it could be made to pass out between the grate bars.

Under (*b*): *The ore may be calcined in hand calciners or mechanical calciners.*—The former are not much used at the present time, as the necessary labour is effectually replaced by mechanical appliances. The hand calciner, which was universally used some years ago, consisted of a long flat bedded reverberatory furnace, with the usual fire box at one end and the outlet flue for the exit of the gases at the opposite end (Figs. 1, 2, and 3). The ore was



FIGS. 1, 2, AND 3.

dropped from a hopper through an opening in the roof on to the bed at the flue end of the furnace, where it was spread out by means of suitable tools worked by men at both sides of the furnace, operating through doors in the side walls.

The conditions in the furnace were intensely oxidising, and it was necessary to stir the ore frequently to prevent it sintering. In the process of stirring, the ore was turned over and moved towards the fire end, thus making room for a fresh charge from the feed hopper. This process of stirring and moving the ore forward towards the fire end was continued until the ore reached close up to the fire box, at which point it was discharged through openings in the bed of the furnace into vaults, or chambers, constructed below, from which—when sufficiently cool—it was removed. The labour required on these furnaces was very heavy and the output small, and, except in unimportant installations, they have given way to furnaces in which the ore is stirred, moved forward, and discharged by mechanical means operated by power. It will be impossible within the limits of this article to describe the many furnaces of this type which have been introduced, and it will suffice to describe one or two which will serve as examples of the class of plant employed.

The McDougall furnace (Fig. 4).—This is very largely used, and consists of a series of flat circular superimposed firebrick hearths, enclosed in a brick-lined cylinder of steel plate. An iron shaft passes centrally up the cylinder through openings in the several hearths, and is caused to revolve by suitable gearing attached either to its upper or lower end. This shaft may be made hollow and cooled by air or water circulation.

One or more iron arms are attached to this shaft above each bed. The arms extend from the shaft to the periphery of the circular beds,

and have attached to them a series of iron plates or ploughs set at a slight angle to the arm. The ore is fed from a hopper on to the top bed near the centre, and the angle of the ploughs is such that, as the arms revolve, they not only turn the ore over, but gradually move it from the centre to the edge of the bed. At one point in the edge of the bed is an opening through which the ore falls on to the second bed. On this bed the ploughs are so set on the arms that the ore travels in the reverse direction and is drawn to the centre of the bed. Here it discharges on to

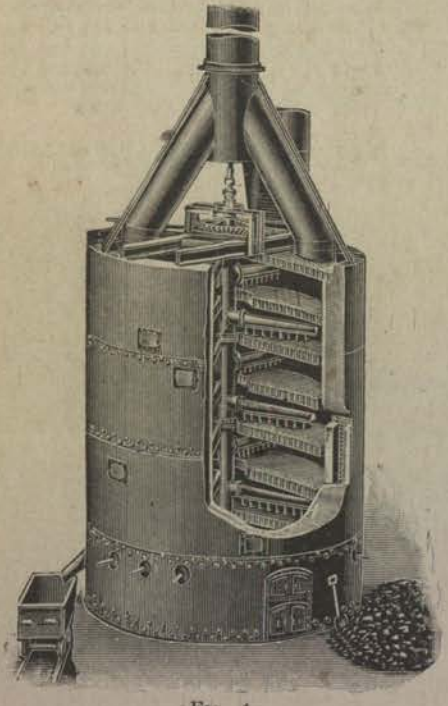


Fig. 4.

the third bed; and so on until it escapes at the bottom of the furnace. The openings through which the ore falls from one bed to the other also serve as flues through which the gases pass upwards through the furnace, finally escaping through a flue above the top bed.

In one modification of this furnace, the flues from the fire box are built in the walls, and are so controlled by dampers that the heat can be conveyed to any one or two of the beds required.

Attached to the lowest bed is a fire box by which the furnace is heated up in order to start it; but, after being once started, little or no fuel is required, as the oxidation of the ore provides sufficient heat throughout the apparatus.

The straight-hearth mechanical furnace.—This type of furnace passes under various distinctive names, according to the several methods adopted for operating the ploughs, and slight modifications in the construction. One such furnace consists of a flat bed about 100 feet long covered with an arch. At one end is the inlet for the ore, and at the opposite end is the outlet. At the ore inlet end is the flue for carrying off the gases, and at the opposite end, but to one side, is a fire box with the inlet to the furnace constructed in the roof of the latter. Other similar fire boxes—one or two in number—are placed at intervals along the length of the furnace. A channel is constructed in the side walls of the furnace and in these a rail is laid. A suitable carriage with wheels resting on the rails stretches from one side of the furnace to the other, and the bearings pass through slots in the two side walls and are carried by the wheels above referred to. To this carriage, suitable ploughs are attached in such manner that, in the course of its travel from one end of the furnace to the other, the ploughs turn the ore over and also move it forward. The carriage is moved by a pair of chains or ropes travelling in the channels formed in the side walls, and at the two ends of the furnace these chains or ropes are carried round wheels sufficiently large in diameter to lead them back under the furnace, thus making them continuous. One pair of these wheels is driven by suitable gearing, thus causing the pair of ropes or chains—and with them the carriage—to travel the whole length of the bed of the furnace, returning through the tunnel under the bed, where rails are laid for supporting the carriage. Two or more such carriages are attached to the ropes, or chains, at equal distances apart. The ore is fed mechanically on to the bed at intervals just as a carriage is about to enter, and the ore is spread, turned over, and moved forward gradually from one end of the furnace to the other. Each time a carriage emerges from the furnace, it draws with it a quantity of calcined ore. The carriage and its attached ploughs are cooled during the passage through the tunnel. The ends of the furnace are closed by light iron doors which hang down vertically and are automatically opened by the passage of the carriage and close themselves as soon as the carriage has passed.

There is yet another method of removing the excess sulphur which has lately been introduced, known as 'pot roasting,' or 'blast roasting.' This method of calcining is advantageously applied to concentrates and fines, and, while it eliminates the sulphur, the heat attained is at the same time sufficiently intense towards the end of the process to cause the ore to partially smelt or sinter together. In this respect it differs entirely from the methods of treatment described above. It has already been pointed out that, in the processes of calcining previously considered, the aim of the smelter is to prevent the ore particles from becoming soft and sintering together, because, under those conditions, oxidation is retarded. In the process now to be considered, however, the final result is a completely sintered mass which requires to be broken up before it can be treated in the smelting furnace. Although one or two modifications of the process have been introduced, the general method of conducting it is as follows:—A cast-iron vessel, capable of holding from 5 to 10 tons of ore mixture, is so supported that at the end of the operation it can be inverted. The usual shape of the vessel is hemispherical, and it is supported by trunnions on a framework at some few feet above the floor. Near the bottom a perforated iron plate is fitted, which is kept in place by an iron bolt passing through it and the bottom of the pot. Under the plate, air—at a

few ounces pressure—can be introduced through a pipe cast on to the pot. The top of the pot is fitted with a light iron hood, connected to the flue system for taking away the gases produced in the operation. This hood is supported in such manner as to allow of its easy removal and replacement. The pot being in the upright position, a thin layer of already calcined ore, in small lumps, is spread on the perforated plate, and upon this a light fire is started and a gentle current of air turned on.

The ore mixture, which must be quite damp, is then charged, a few shovels full at a time, and, as the fire burns up through the combustion of the sulphur, the ore is put in in gradually increasing quantities until the pot is full, the supply of air being increased as the filling up is proceeded with. When the pot is full, the hood is lowered into place, and the operation then proceeds by itself. The air current causes a rapid oxidation, and the fire gradually rises from the bottom upwards; finally, the temperature reaches the point at which slag formation commences, and the whole mass sinters together. When this stage is completed, the hood is lifted or moved away, and the pot is rotated until the sintered mass falls out on to the floor below, where it is broken up into pieces of a suitable size for the smelting operation to follow. In carrying out this process, it is essential that the ore mixture treated should contain all the necessary elements for the production of slag. Thus, for instance, if the silica content of the ore is low and not sufficient to combine with the iron oxide produced in the operation, then silica, in some form, must be added to the ore before it is charged into the pot.

After the sulphur in the ore mixture has been reduced to the requisite amount, the ore is ready to be smelted. For this operation one of two distinctly different types of furnace are used; these are:

(1) Blast furnace. (2) Reverberatory furnace.

The choice between these two methods of carrying on the smelting operation depends on a variety of circumstances, all of which must have proper consideration, but the following are the chief points, viz.: If the ore is to be smelted in the state of fines or concentrates, it is unsuitable for blast-furnace treatment, while it is eminently suitable for the reverberatory furnace. On the other hand, rough ore is unsuitable for reverberatory-furnace smelting.

Blast-furnace smelting.—The furnace used may be built of brick, but is more generally, nowadays, constructed with water-cooled walls of steel plate (Fig. 5), each section of which is termed a jacket. In the smaller furnaces the horizontal section is circular, but in the ordinary sized and larger furnaces the section is always rectangular. As the working of this type of furnace is—as its name implies—dependent upon an air blast projected into the interior, the width of the furnace is limited by the strength of the blast which is required to penetrate the charge from the sides to the centre of the furnace, while the length of the furnace is only limited by the capacity required. The increase in length is obtained by clamping together two or more of the jackets on each side, thus extending the longer axis of the furnace.

The jackets stand on a thick cast-iron plate carried on iron supports. In some cases these jackets are only used in the lower part of the furnace, all the upper part being constructed of brick, but the brickwork may, in certain cases, be advantageously replaced with a second tier of jackets, reaching up to the feed floor. Above the feed floor the furnace is continued in the form of a covered-in brick chamber with lifting doors at each side and an outlet in the roof of the chamber, connecting, by means of a suitable iron flue, to the general flue system of the works.

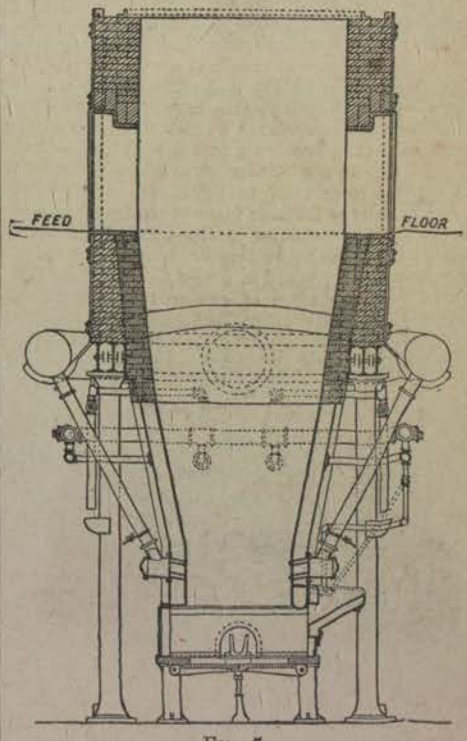


FIG. 5.

Through the doors the charge, consisting of a proper mixture of ore—both raw and calcined, or partially calcined ore—is introduced. To this ore mixture there is also added such flux, either limestone or silicious material, and the necessary amount of coke as is required to form a suitable smelting mixture. As previously indicated, the object of this is to produce a matte of the desired grade and a slag which shall be as free from copper as possible and which shall be of such fusibility as to flow readily from the furnace. On the lower or working floor, the furnace is provided, either at the ends or sides, with one or more spouts through which the molten products of the smelting operation flow. Except in very large furnaces, only one such spout is used at a time, and if more than one is fitted, it is with the object of having one in reserve in case of a stoppage to the one in use.

The side jackets of the furnace are provided with circular openings (tuyères) passing from

the outer to the inner surface. When the jackets are set up, these tuyères form a horizontal line of openings on each side of the furnace. The blast is brought down from the air main by light iron piping to the tuyères, and through these it passes to the interior of the furnace.

The blast, at a pressure of 10–50 or 60 oz. per sq. inch, is generated by a suitable blowing machine, which must be of the positive, and not the fan, type. A plentiful supply of water is circulated through all the jackets, and the overflow pipes from these, carrying away the hot water, discharge into sinks or launders.

The products of the smelting operation performed in this furnace flow out through the spout above described into the settler. In the case of small furnaces, this is a square cast-iron vessel open at the top and mounted on wheels to allow of easy replacement. It is furnished with a cast-iron spout at its upper edge through which the slag overflows, and is provided with a tap hole near the bottom from which the matte is tapped from time to time. In the case of larger furnaces for this form of settler, there is substituted a circular tank, formed of steel plates lined with refractory material, placed permanently in position under the spout of the furnace. This form of settler may be 10 or more feet in diameter, and, like the smaller pattern mentioned above, is provided with a slag spout near the top and a tap hole near the bottom.

In the settler, a thorough separation of the slag and matte takes place: the matte, having the higher specific gravity, falling to the bottom of the vessel and the lighter slag rising to the top, where it overflows through the spout into suitable pots provided for its removal to the slag dump. From time to time the matte is tapped off through the tap hole at the bottom of the settler. The working of this type of furnace proceeds continuously, fresh ore charges being dumped in at the top at intervals, while a constant flow of slag and matte passes out through the spout.

Reverberatory-furnace smelting.—The furnace used is essentially different both in construction and method of working from the one previously described. In the blast furnace, the fuel—coke—is burnt in contact with the materials to be smelted, and the intense heat required for the operation is obtained by urging the combustion of the fuel by means of an air blast. In the reverberatory furnace the material to be smelted occupies one compartment of the furnace, while the fuel—coal or wood—is burnt in another. The draught required for the combustion of the fuel is quite moderate, and is obtained by a chimney of suitable height and area. The working bed of the furnace in plan is a parallelogram (Fig. 6) with rounded corners. At one end, and separated from it by a low partition, is the fire box, in which the fuel is consumed. At the opposite end is the outlet flue connecting with the chimney. A brick arch extends from the back wall of the fire box to the flue. This arches the furnace across from side wall to side wall, and is constructed with a fall from the fire-box end to the flue end of the furnace. The partition, or bridge, as it is termed, to which reference is made above as separating the working bed from the fire box, reaches to such a height above the bed that an opening is left between its top surface and the roof of the furnace. Through this opening above the bridge, the flame from the burning fuel passes over the bed on its way to the outlet flue. The side walls of the furnace are pierced with a number of openings used in working the furnace for spreading the ore charge, drawing off the slag, &c., and one opening is cut down to the lowest point of the bed for tapping the matte.

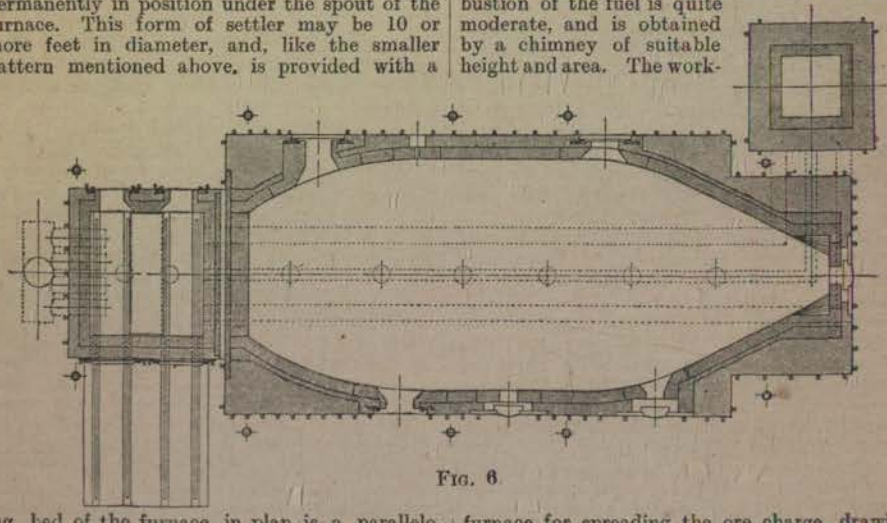


FIG. 6.

The furnace walls and roof are constructed of highly refractory bricks with an outside casing of ordinary bricks, and the whole is bound together with steel girders placed vertically and tied together from one side to the other by iron tie rods. The working bottom is variously constructed. It may be formed of highly refractory bricks, or of silicious sand or crushed quartz. If formed of brick, these are laid on a layer of brasque in the form of a slightly curved invert arch, and with as close a joint as possible; when the furnace has been dried by means of a slow fire, it is ready for work.

In the case of the sand or crushed quartz bottom, however, the procedure is different.

After the furnace is completed, but without its refractory working bottom, the brickwork is thoroughly dried by a slow fire, then the heat is very gradually raised and a quantity of sand, or quartz, is thrown in and heated to a dull-red heat. When this stage is reached, the material is formed roughly into the shape required for the bottom by means of suitable tools. The fire is now urged to the highest point possible, so as to slightly frit the particles of sand or quartz, at least on the surface. When this is effected, the furnace is cooled and a small charge of some easily fusible slag is carefully spread over the surface. The heat is again raised so as to smelt this slag, which is absorbed by the bottom; this is repeated once or twice, when the furnace will be ready for a light charge of its ordinary ore mixture, which is gradually increased until the full-weight charge is reached. Charging of this furnace takes place through one or more openings in the roof from hoppers supported above. Assuming that the furnace is heated up to the required temperature, a charge of ore mixture is dropped from the hoppers above through the openings in the roof. This is then spread over the bed by means of suitable tools operated by men working through the side and front doors. When this operation is completed, the doors are closed and the fire attended to so as to raise the temperature of the furnace as rapidly as possible to full heat. The charge is occasionally stirred, if necessary, to remove any agglomerated masses from the bottom of the furnace, and finally, a molten bath is obtained composed of two distinct layers—the matte forming the bottom layer, and the slag floating upon it. When this stage is reached, another charge may be dropped and treated in the same way; and this may be repeated from time to time until the furnace is full of molten slag and matte. A side door and end door are opened and the slag allowed to run off, and towards the end, this is drawn off by means of tools handled by the furnace-men until nearly all the slag has been removed. The tap hole is then carefully opened, and this being at the bottom of the furnace, the matte flows through it and is led by a launder into a ladle or into moulds placed on the floor to receive it. When nearly all the matte has been run off, the tap hole is again closed and made secure, fresh charges are dropped, and the operations repeated.

The slag may be received in ladles mounted on wheels, and in these may be removed to the dump, or it may be received in sand moulds formed on the floor of the furnace house; when cool, it may be broken up and removed to the dump, or it may be run into a stream of water, and thus granulated and removed.

The object attained in this operation in the reverberatory furnace is the same as with the blast furnace, viz. the production of the proper grade matte and a slag of easy fusibility reasonably free from copper.

Pyritic smelting.—This method of working, which has been introduced of late years, secures in one operation what, in the preceding descriptions, is attained in two processes carried on in separate appliances. It has been shown that, in order to produce a proper grade of matte, a certain proportion of sulphur must be oxidised to sulphur dioxide, and that, accompanying this action, a portion of the iron sulphide must also be oxidised. It has also been shown that, in ordinary working, this preliminary treatment and the actual smelting of the ore are carried out as two distinct operations in two entirely different classes of plant. It has also been indicated that, in the smelting operation proper, the high temperature necessary is obtained by the combustion of carbonaceous fuel. In pyritic smelting, the two processes referred to above are carried out as one operation in one furnace, and the high temperature necessary is derived from the rapid oxidation of the sulphur and iron (chiefly the latter) contained in the ore itself. While this method of working is of the highest importance from an economical point of view, it is of somewhat limited application, owing to the fact that comparatively few mines produce ore which—as regards its physical condition and chemical constitution—is suitable for this method of treatment.

The process is carried out in blast furnaces, and for its successful operation demands a larger volume of air per unit of time than the ordinary smelting process and an ore mixture in which the pyritic material is present in fairly large masses. The silica must be, for the most part, free silica (quartz), and not combined with earthy bases as silicates. Under these circumstances, the ore may be satisfactorily smelted, producing the required matte and slag with the consumption of but 1 to 3 p.c. of coke. A small amount of coke appears at present to be necessary in order to keep the charge open.

II. *Treatment of the matte for the production of crude copper.*—It has already been pointed out that matte consists of cuprous sulphide Cu_2S, with varying proportions of iron sulphide FeS, and the carrying out of the stage which is now to be considered involves the elimination of the sulphur and iron, while the copper is left in the metallic state. The process is carried out by different methods, the chief of which will now be considered. In all of these the operation is performed in two stages, although, in some cases, these follow one immediately after the other and in the same apparatus, while in others the stages are performed as two separate operations and in two or more separate furnaces. The first stage in each case consists in the removal of the FeS with the production of Cu_2S, and the second stage treats the Cu_2S with the production of metallic copper. The carrying out of the first stage depends upon the fact that, when matte is exposed to oxidising conditions, the iron sulphide is the first of its constituents to be decomposed, the sulphur being oxidised to sulphur dioxide. The resulting iron oxide is then caused to combine with silica, forming a slag which can be removed from the residual cuprous sulphide.

The second stage in the process depends upon one or more of the reactions represented by the following equations:—

$$Cu_2S+2Cu_2O=6Cu+SO_2;$$
$$Cu_2S+2CuO=4Cu+SO_2;$$
$$Cu_2S+CuSO_4=3Cu+2SO_2;$$

the first being the most important as representing the change which takes place in the largest proportion of the material. The reactions indicated are effected by bringing the

several chemical compounds together in a molten condition. The oxidised compounds may be added to the molten Cu_2S from outside sources or may be, and generally are, produced by the oxidation of a portion of the cuprous sulphide itself.

The reactions outlined above are, at the present day, almost always brought about by what is termed the 'converter process,' also named 'Bessemerising,' the former name derived from the designation of the vessel in which the operation is performed, viz. converter, and the latter from the name of the distinguished inventor, Sir Henry Bessemer, who had many years previously applied a similar method and plant to the production of wrought iron and steel from cast iron.

The converter consists essentially of a vessel formed of steel or iron plate, with a thick lining, generally of highly silicious rock to which a small quantity of clay has been added, sufficient only to give the necessary coherence. The vessel is provided with a suitable aperture serving the purpose of a charging opening through which the matte to be operated upon is poured in a molten condition, also as an outlet through which the products of the operation are poured, as well as being an escape for the gases produced in the process. The vessel is supported on horizontal trunnions or on friction rollers at some little distance above the working floor of the furnace house, and is capable of being rotated by electric or by hydraulic power (*Fig.* 7). The form of the vessel is more or less

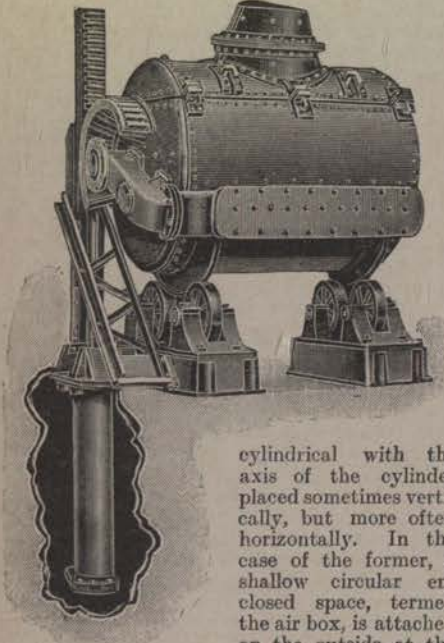


FIG. 7.

cylindrical with the axis of the cylinder placed sometimes vertically, but more often horizontally. In the case of the former, a shallow circular enclosed space, termed the air box, is attached on the outside at the bottom of the vessel. In the latter form, this air box takes the shape of a long rectangular box attached horizontally to the outside of the converter. From these boxes holes are led through the plates forming the casing of the converter, and are continued through the lining to the interior. Air, at a pressure of from 8 to 12 lbs. per square inch, is supplied to the air boxes as required, and the supply is controlled by suitable valves. Charging of the converter with matte is effected by means of a launder direct from the furnace, or settler, or by tapping these first into a steel ladle handled by an overhead crane which conveys it to the converter and pours it.

The converter, having been lined and the lining dried by a slow fire, is placed upon the stand and connected up to the air main. A charge of molten matte is then poured in, the converter having been tilted into a suitable position for receiving it. The air being turned on, the converter is then tilted over so that the tuyères are brought beneath the surface of the matte, and the air, being forced through the molten sulphides, causes a rapid oxidation of the constituents of the iron sulphide. The sulphur is oxidised in this way to sulphur dioxide and the iron to oxide, which is immediately converted to silicate by combination with the silica of the lining. As the oxidation proceeds, the temperature of the charge increases and the operation is continued until practically the whole of the iron sulphide has been decomposed, and the contents of the converter consist of cuprous sulphide and slag. The converter is now turned over and the slag run off into pots or moulds, and when this is done, it is again turned into the blowing position, when the second stage of the oxidation is commenced. The passage of the air through the molten cuprous sulphide brings about the oxidation of a part of that material to cuprous oxide, which immediately reacts upon unaltered cuprous sulphide with the production of an equivalent quantity of metallic copper, in accordance with the reactions given on page 133. This action continues until all the cuprous sulphide has been decomposed and the contents of the converter consist of metallic copper; any small quantity of slag which may be on the surface is removed by turning down the vessel and skimming off. The metallic copper is then poured into moulds of the shape required by tilting the converter. As the slags produced in the operation are likely to contain intermixed shots and splashes of cuprous sulphide, they are resmelted in the furnace plant in which the matte was produced in the first place. As soon as the copper has been poured, the converter is ready to receive another charge, and the operations are repeated. When several charges have been put through (the number depending upon the nature of the rock material of which the lining is formed and the care exercised in ramming it into place), the lining becomes too thin for further use; the converter is therefore removed to the relining department by means of the crane, the old lining is taken out and a fresh one put in, when, after drying, it is again ready for use.

Another method for the production of metallic copper from the matte is conducted entirely in reverberatory furnaces, and is sometimes employed where the output does not justify the more expensive converter plant previously described. In this method of working, the first stage, viz. the removal of the iron sulphide of the matte by oxidation of

its constituent elements, is effected by smelting the material with a proper proportion of calcined matte together with silica sufficient to form a silicate of iron slag with the iron oxide; or the matte may be smelted with oxidised copper ore, silica being also present. In either case, the result is that the iron sulphide is decomposed, the sulphur passing from the furnace as sulphur dioxide, and the iron forming, with the added silica, a slag, which is removed. The contents of the furnace at this stage consist chiefly of cuprous sulphide, Cu_2S. Currents of heated air are directed over the surface of the molten bath, with the resulting formation of cuprous oxide and the concurrent reaction between this and the unchanged cuprous sulphide results in the production of metallic copper, in accordance with the equations set out on page 133. When this reaction has extended to the whole contents of the furnace, the heat is raised and the metallic copper is tapped out into moulds.

In one method of working, known as the direct process, the furnace is tapped at the stage when the product is practically cuprous sulphide; when cold, a portion of this is finely crushed and completely oxidised by calcination in furnaces similar to those used for calcining ore fines. The calcined material is then mixed with the crushed uncalcined portion, and the reaction between Cu_2S and Cu_2O is brought about as indicated in the equation on page 133, by smelting the mixture in a reverberatory furnace of the same general construction as that used in the earlier stage of the process.

III. *Refining.*—The method of treatment to be adopted in this operation depends upon whether (*a*) the copper is practically free from gold and silver and from deleterious elements; (*b*) the copper contains appreciable quantities of gold and silver, or contains undue quantities of deleterious elements.

If the metallic copper produced by the operations previously described under I. and II. comes under the description (*a*) above, it can be refined by furnace treatment only; if it comes under (*b*) it must be refined electrolytically in order to recover the gold and silver or to obtain it free from the impurities.

Under (*a*), the furnace employed is of the reverberatory type, and the removal of the impurities is effected by slowly melting the pigs of copper under highly oxidising conditions, and maintaining the bath of molten copper under this condition until the impurities are oxidised and removed, either by volatilisation or by passing as oxides into the copper silicate slag formed. The oxidation of the impurities is facilitated by the fact that metallic copper has the property of dissolving a small proportion of cuprous oxide, which compound is brought into contact with the elements to be oxidised under the very favourable condition of fluidity.

The oxidising condition of the bath of molten copper is maintained until the impurities are removed, as far as practicable, and the copper contains a maximum quantity of dissolved cuprous oxide. In this condition the metal is said to be 'dry.' After removal of the slag, the next stage consists in reducing the greater portion of the dissolved cuprous oxide, which is effected by depressing poles of green wood below the surface of the bath of metal, when considerable agitation takes place and the cuprous oxide is subjected to the reducing action of the gases given off by the pole.

The process is continued until only a small quantity of cuprous oxide remains, and the copper attains the physical condition known as 'tough pitch,' when it is ladled out into moulds of any required shape.

Under (*b*), the copper is refined electrolytically. This process depends for its operation upon the fact that if an electric current is caused to pass through a solution of copper sulphate, the copper in the solution is deposited at the cathode, while the acid is set free at the anode. If the anode is composed of metallic copper, then the acid set free on its surface immediately dissolves an equivalent portion of copper which passes into solution, and is, in turn, deposited at the cathode, and the process thus becomes continuous so long as the current passes and there is copper at the anode to be dissolved. Assuming that the solution of copper sulphate is properly made up and maintained, and the voltage and current are suitably adjusted, then *only* copper will be deposited at the cathode, while the gold and silver and all the impurities contained in the copper anodes will either remain as insoluble slime, collected at the bottom of the vessel in which the operation is conducted, or will pass into the electrolyte. Gold, silver, and lead pass entirely into the insoluble slime; other elements, such as iron and nickel, pass wholly into the solution, and others again are to be found partly in the slime and partly in the electrolyte. The cathode surface is, to start with, a very thin sheet of electro-deposited copper, and when—as the result of the operation—sufficient copper has accumulated upon its surfaces, it is removed from the bath and is ready for melting and casting into any required shape. In practice, a number of anode plates are hung in a lead-lined wooden tank, and are suitably connected to the positive lead. Alternating with these anode plates are hung the cathode sheets, connected in parallel with the negative lead. A large number of tanks are connected in series, and the current is passed through the whole set of tanks. The electrolyte is caused to circulate through the whole series, and, after it has been in use for some time, a certain proportion must be removed regularly for purification. A quantity of anode copper remains undissolved, and when the tank is to be cleaned, this is taken out for remelting into anodes, the solution is run off, and the slime is removed. This latter is washed and dried, any large particles of copper removed by sieving, and the fine slime is then treated for the recovery of any silver or gold which it may contain.

Wet methods. These are of very limited application, and only adapted to very poor ores. They depend upon the fact that some copper minerals are decomposed and rendered soluble by certain acids and ferruginous salts, as, for instance, oxidised ore in sulphuric acid, and some copper and iron sulphides by solutions of ferric sulphate and chloride. When such solutions, separated from the gangue material of the ore by filtration, are brought into contact with metallic iron, the copper contained in the solution is precipitated on the iron and is removed from time to time. After removal, it is washed

and melted and then refined as previously described.

Another method of rendering the copper mineral soluble, which is sometimes employed, is to calcine the finely crushed ore with salt at a low temperature. On treating this afterwards with water, the soluble copper salts resulting from the operation are removed and the solution, on being treated with metallic iron, yields the copper in the metallic state, as in the methods previously mentioned. T. C. C.

Compounds of Copper.

Oxides. Five oxides of copper are said to be known: the quadrantoxide Cu_4O, the trientoxide Cu_3O, the sub- or hemi-oxide Cu_2O, the monoxide CuO, and the peroxide CuO_2. Other oxides have been described, but their existence is not proved.

Copper quadrantoxide is stated to be formed by adding a solution of copper sulphate to a cooled dilute solution of stannous chloride in caustic potash (Rose, Pogg. Ann. 1861, 120, 1). It is an olive-green powder, which rapidly absorbs oxygen from the air. According to Moser (Zeitsch. anorg. Chem. 1909, 64, 200), this product is really a mixture of cuprous oxide and copper.

Copper trientoxide is obtained by heating cupric oxide at 1500°–2000° as a hard yellowish mass. It is unaffected by any acid except hydrofluoric (Bailey and Hopkins, Chem. Soc. Trans. 1890, 269).

Copper suboxide, or hemioxide, red oxide of copper, cuprous oxide Cu_2O, occurs native as *cuprite* or red copper ore, and as *chalcotrichite*.

It may be prepared (1) by heating finely divided copper in air below a red heat; (2) by gently heating a mixture of 5 parts cuprous chloride and 3 parts sodium carbonate in a covered crucible, and separating the oxide by lixiviation; (3) by reduction of an alkaline solution of a copper salt by sugar or certain other organic bodies, as in Fehling's solution; (4) by heating in a covered crucible a mixture of 5 parts copper monoxide and 4 parts copper filings; (5) by the electrolysis of copper sulphate solutions under certain conditions (Miller, J. Phys. Chem. 1909, 256; Gillett, *ibid.* 1909, 332).

This oxide is decomposed by most acids into a cupric salt and copper; hydrochloric acid, however, converts it into cuprous chloride.

Cuprous oxide fuses at a bright-red heat. It dissolves in metallic copper and renders it brittle or 'dry' when present in quantity. As much as 4·6 p.c. has been found by Abel in very dry copper, and, according to Watson (J. Soc. Chem. Ind. 1883, 154), from 1 to 2½ p.c. is present in ordinarily good copper.

It is largely used in the manufacture of *ruby glass*, and for the production of a red glaze on pottery (Louth and Dutailly, Mon. Ceram. et Verr. 19, 237), and, together with the black oxide, forms one of the so-called *copper paints* used for painting ships' bottoms.

The hydrated oxide is produced by the action of alkali on cuprous chloride. The yellow precipitate thus formed is not a definite hydrate, but is a colloidal form of the oxide with an indefinite amount of water (Gröger, Chem. Zeit. Rep. 1902, 197). It is a powerful reducing agent, especially in ammoniacal solution. This solution, which is colourless, immediately becomes blue from the formation of the monoxide on exposure to the atmosphere, and thus forms a delicate test for oxygen. The hydrated oxide dissolves in a concentrated solution of magnesium chloride.

This oxide is produced in Hoepfner's process for extracting copper from ores, &c., with cupric chloride solution. Cuprous chloride is formed and treated with alkali to obtain cuprous oxide (J. Soc. Chem. Ind. 1893, 932; Eng. Pat. 18900. 1892).

Copper monoxide, cupric oxide, black oxide of copper, 'copper oxide' CuO, occurs as *melaconite* or *black copper*, especially at Lake Superior.

It may be prepared by heating the nitrate or carbonate to dull redness or the sulphate to intense redness. The decomposition of the sulphate is the basis of Adcock's process for the preparation of the oxide direct from the natural carbonate or sulphate (Eng. Pat. 11678, 1900). The copper oxide used for organic analysis, &c., may be prepared by moistening copper scale (the mixture of suboxide and black oxide obtained while working copper sheet, &c.) with nitric acid, and igniting.

An electrolytic method of preparing the oxide has been described by Miller (J. physikal. Chem. 1909, 256); and by Luckow (Zeitsch. Elektrochem. 1897, 482).

Copper oxide is a black powder which agglomerates when heated, and fuses at the melting-point of copper, forming cuprous oxide, or Cu_2O, according to the temperature. It can be made to crystallise in regular tetrahedra. It is slightly hygroscopic, especially when in powder. When heated with organic substances or certain gases, it is reduced to metal. The metal produced by reduction in hydrogen always contains that gas, but if the oxide be reduced in formic acid vapour, the metal is quite free from hydrogen and is suitable for organic analysis (Weyl. Ber. 15, 1139).

It dissolves in acids with formation of cupric salts. In oils, &c., it is soluble to some extent; it is for this reason that copper cooking vessels require such constant cleansing.

Copper oxide is used for ultimate organic analysis; to make green and blue glass and glazes, and to some extent as a pigment. It has also been used as one electrode of a galvanic cell (*v.* Lelande and Chaperon, Bull. Soc. chim. [2] 49, 173).

Hydrated copper oxide $CuO{\cdot}H_2O$ may be prepared by precipitating a solution of a copper salt by addition of alkali and washing rapidly. When heated with water, it becomes black and amorphous.

A colloidal form of the oxide has been obtained by Paal and Leuze (Ber. 1906, 1545), which gives blue-violet solutions, and when dry retains its solubility indefinitely.

The hydrated oxide is used as a blue pigment by paper stainers, but becomes green on exposure. It corresponds closely with certain of the highly basic carbonates sold as *verditers*. According to Dumas, it is best prepared as follows: 6 parts of copper sulphate are dissolved in water and mixed with a solution of 3 parts of calcium chloride. The clear liquid is decanted

from the precipitated calcium sulphate and is mixed with 1½ parts of lime made into a cream with water. The greenish precipitate is collected, washed, and mixed with one-fourth its weight of slaked lime and as much pearl ash, and to render the colour more permanent, one-fourth its weight of ammonium chloride and one-half its weight of copper sulphate are usually added.

The hydrated oxide dissolves in ammonia, the saturated solution in strong ammonia being known as 'Schweitzer's reagent,' or *cuprammonium*. This solution has the property of gradually dissolving *cellulose* with formation of a viscid solution which is used for the preparation of the 'Willesden papers,' and for the production of 'artificial silk' on the large scale. This process consists in injecting the copper-cellulose solution into strong solutions of alkali or acid. In either case, coagulation takes place with formation of a fibre of cellulose corresponding in thickness to the diameter of the jet.

Cuprammonium solutions are prepared on the large scale by the joint action of oxygen and ammonia on metallic copper at temperatures near 0° (Schaefer, U.S. Pat. 884298, 1908; Bronnert, Frémery, and Urban, Eng. Pat. 1763, 1900; Lecœur, Fr. Pat. 374277, 1906).

Bellot has patented a continuous process of manufacture, using a series of closed vessels (Fr. Pat. 335207, 1903).

The solution should be purified by dialysis, as the presence of crystalline salt favours its decomposition (Lecœur, Fr. Pat. 362986, 1906). Addition of 1–2 p.c. of polyhydric alcohols, carbohydrates, gum, &c., to cuprammonium solutions increases their stability and prevents the deposition of cupric hydroxide (Friedrich, Eng. Pat. 4104, 1909), and the presence of such substances facilitates manufacture of the solution, making it possible to employ copper concentrations up to 5 p.c. without cooling (Fr. Pat. 399911, 1909).

Chattaway has shown (Proc. Roy. Soc. 1908, 80, A, 88) that by the reduction of a cuprammonium solution with aromatic hydrazines, copper mirrors can be deposited on glass.

Dawson states that a solution of cupric hydroxide in ammonia contains copper as the base $Cu(NH_3)_4(OH)_2$ (Zeitsch. physikal. Chem. 69, 110). (For a general discussion of the constitution of cuprammonium salts, *see* Horn and Taylor (Amer. Chem. J. 1904, 253); and Horn (*ibid.* 1907, 475).)

Copper dioxide, copper peroxide CuO_2, is obtained by the action of hydrogen peroxide on cupric hydroxide in neutral solution at 0° (Krüss, Ber. 1884, 17, 2593; Moser, Zeitsch. anorg. Chem. 1907, 54, 121). The crystalline precipitate is washed with water, alcohol, and ether at 0°, and dried *in vacuô*. It has a yellowish-brown colour, and decomposes at 180°, forming cupric oxide.

SALTS. Two series of copper salts are known, *cuprous* and *cupric*. The former are mostly insoluble in water, and are of but little commercial importance. They act as powerful reducing agents and readily pass into the cupric condition. Cupric salts are mostly soluble, and are of wide application.

Cuprous chloride Cu_2Cl_2 may be prepared, amongst other methods, by boiling cupric chloride with hydrochloric acid and copper turnings. On addition of water it is precipitated in white crystals.

Zuloaga has suggested (Rev. Chim. Ind. 1900, 107) that the cuprous chloride solution used in the extraction of silver from its ores should be prepared by mixing solutions of cupric sulphite and of cupric sulphate and sodium chloride.

Cuprous chloride melts below a red heat into a yellow transparent mass. The dry crystals become yellowish on exposure to light; if moist, they acquire a dirty-violet tinge. Plates of copper coated with this chloride by the action of chlorine will take photographic impressions, but cannot be made to withstand exposure to light (*v.* Carlemann, J. pr. Chem. 63, 475; and Priwoznik, Dingl. poly. J. 221, 38).

Cuprous chloride combines with ammonia to form three compounds

$Cu_2Cl_2{\cdot}NH_3$, $Cu_2Cl_2{\cdot}3NH_3$, $Cu_2Cl_2{\cdot}6NH_3$.

Cuprous bromide and iodide form compounds analogous to the last two (Lloyd, J. Phys. Chem. 1908, 398).

The hydrochloric acid solution, when exposed to air, absorbs oxygen and acquires a brown colour, subsequently depositing a pale bluish-green insoluble copper oxychloride

$$CuCl_2{\cdot}3CuO{,}4H_2O.$$

An identical substance used as a pigment, and known as *Brunswick green*, is prepared by boiling a solution of copper sulphate with a small quantity of bleaching powder solution; or by moistening copper turnings with hydrochloric acid or ammonium chloride with free exposure to air. It occurs in nature as *atacamite*.

The use of the oxychloride in preference to the sulphate for destroying mould on vines, &c., is recommended. 200–250 grams per litre of water are taken (Deletrez, J. Soc. Chem. Ind. 1909, 438).

When a solution of cuprous chloride in potassium chloride, acidified with hydrochloric acid, is treated with acetylene, a yellow precipitate of $Cu_2Cl_2{\cdot}C_2H_2$ is formed. Other compounds containing copper oxide or potassium chloride can be obtained by varying the conditions (Chavastelon, Compt. rend. 132, 1489).

Acetylene reacts with solutions of cuprous chloride in ammonia to form a blood-red precipitate of *cuprous acetylide*, which, on dehydration, has the formula Cu_2C_2, and is highly explosive (Scheiber, Ber. 1908, 3816). Its decomposition by acids has been used as a means of preparing pure acetylene. A colloidal solution of copper acetylide has been prepared by Küspert (Zeitsch. anorg. Chem. 34, 453) (*v.* ACETYLENE).

Cuprous bromide Cu_2Br_2 is obtained by the union of its elements or by boiling a solution of cupric bromide with copper, and forms a brown crystalline mass.

Cuprous iodide is the only known iodide of copper, and is obtained as a white precipitate by adding potassium iodide to a solution of copper sulphate containing ferrous sulphate or sulphurous acid. It has a sp.gr. 5·653 at 15° (Spring, Rec. trav. chim. 1901, 79), melts without decomposition at 628°, and is practically insoluble in water.

Cuprous sulphate Cu_2SO_4 can be prepared

by the action of dry dimethyl sulphate on dry powdered cuprous oxide (Recoura, Compt. rend. 148, 1909, 1105). A compound of cuprous sulphate and carbon monoxide $Cu_2SO_4 \cdot 2CO, H_2O$ has been obtained by Joannis (*ibid.* 1903, 615), by reducing cuprammonium sulphate with hydroxylamine. Péchard has made ammonio-cuprous sulphate $Cu_2SO_4 \cdot 4NH_3$ (*ibid.* 1903, 504).

Cuprous sulphide Cu_2S occurs as *chalcoite* or *copper glance*. It may be prepared by heating copper to redness in sulphur vapour, or by heating a mixture of copper and sulphur. It has no commercial application.

Cupric chloride $CuCl_2$ may be prepared as a fused, liver-coloured, anhydrous mass by heating copper in excess of chlorine. In solution it may be prepared by dissolving the oxide in hydrochloric acid. It crystallises in grass-green prisms or needles containing 2 molecules of water. They become pale-blue when dried *in vacuô*. The anhydrous salt is obtained on gradual addition of a large excess of conc. sulphuric acid to a solution of the chloride (Viard, Compt. rend. 1902, 135, 168).

Cupric chloride is very deliquescent, and is soluble in alcohol. When a small quantity of potash is added to the aqueous solution, a pale-blue basic oxychloride $2CuO \cdot CuCl_2, 4H_2O$ is precipitated. It turns to a black anhydrous powder when heated, but again becomes green with absorption of 3 molecules of water when moistened. It is an intermediate product in the manufacture of *verditer* (*v. Copper carbonates*).

Cupric chloride is used in calico printing, in the manufacture of *methyl violet*, and for the oxidation of *Cutch colours*.

Green has shown that the chloride is a very effective disinfectant (Zeitsch. für Hygiene, 1893, 495).

Cupric bromide $CuBr_2$ is obtained by dissolving cupric oxide in hydrobromic acid and evaporating *in vacuô*. It is dark-coloured, very deliquescent, and, when heated, decomposes into cuprous bromide and bromine. It is used as an intensifier in photography, and for that purpose is made by dissolving in water a mixture of anhydrous copper sulphate and potassium bromide (Akt. Ges. f. Anilinfabr. D. R. P. 201168, 1907).

Cupric sulphate, *Blue vitriol* $CuSO_4, 5H_2O$, occurs naturally at Copaquire, Chile, the rock containing over 12 p.c. of the hydrated salt (Walker, Eng. and Min. J. 1903, 710). This salt may be prepared by dissolving copper or its oxide in sulphuric acid.

It is prepared on the large scale from metallic copper in the following way: Old copper plates from the sheathing of ships, &c. are heated to strong redness in a reverberatory furnace, and an excess of sulphur is thrown in and the doors are closed. When combination is complete, the doors are reopened and the heat is raised to dull redness to oxidise the sulphide into sulphate. The mass, while hot, is thrown into dilute sulphuric acid, allowed to settle, decanted, concentrated, and crystallised. The sulphate so produced is of considerable purity. *Coarse copper* and *copper glance* or other sulphurous copper ores are similarly treated. Pauffin and Couvert have patented a process for the direct manufacture of the sulphate from the metal (Fr. Pat. 399413, 1909). (*See* also Walker, U.S. Pat. 788862, 1905.)

When much iron is present, as in most copper ores and especially in copper pyrites, it would be impossible to separate the copper and ferrous sulphates by crystallisation, because, although copper sulphate crystallises normally with 5 molecules of water, it forms, in presence of ferrous sulphate, crystals isomorphous with that salt and containing 7 molecules of water. By carefully adjusting the temperature at which the sulphide is roasted, however, the iron salt may be converted into the oxide while the copper sulphate remains almost unaffected. The iron may be removed by heating the solution of the sulphates to 180° in a copper boiler under pressure. Ferrous sulphate crystallises out and is filtered off (Gin, Fr. Pat. 328800, 1903). The iron may be oxidised and thus separated from the copper by boiling the solution with a little nitric acid. It may also be precipitated as oxide by boiling with copper oxide, or by boiling with lead peroxide with subsequent addition of a little barium carbonate.

Crude copper or the ore may be roasted in air, and then treated with sulphur dioxide to form the sulphate (Gin, Zeitsch. angew. Chem. 1903, 566; Eng. Pat. 5230, 1903).

Darier has patented a process in which cupric chloride is formed by the action of chlorine and water on the metal, and is then decomposed by sulphuric acid, with formation of the sulphate and regeneration of hydrochloric acid (Fr. Pat. 350421, 1904).

When the sulphate is required for purposes where the presence of iron is not injurious, such liquors, or the mother liquors from which the purer salt has been separated, may be at once crystallised out, with the formation of crystals containing both iron and copper. Much of the '*agricultural copper sulphate*' is of this class. The '*Salzburg vitriol*,' prepared at Buxweiler, also contains both iron and copper. According to Lefort (Compt. rend. 26, 185), it consists of $CuSO_4 \cdot 3FeSO_4, 28H_2O$. '*Cyprian vitriol*,' prepared at Chessy from zinciferous copper ores, forms blue rhombic prisms, which contain, according to Lefort, $CuSO_4 \cdot 3ZnSO_4, 28H_2O$.

The copper may be separated from the ferrous mother liquors by placing them in vats containing iron plates upon which the copper is slowly deposited.

Apparatus for the solution of copper oxide in sulphuric acid upon a large scale has been described by Coste (Fr. Pat. 392617, 1908). If copper be known to contain silver or gold, as is the case with that from the Harz, it is treated with sulphuric acid diluted with its own volume of water, the copper being thus dissolved while the silver and gold are unattacked.

Argentiferous copper ores are roasted in a reverberatory furnace, and added in small charges to sulphuric acid and digested until the solution contains but little free acid. The solution is then decanted from the precipitated lead and gold, and is concentrated and run into lead-lined tanks containing plates of copper, upon which all the *silver* and part of the *antimony* and *arsenic* are deposited, while the greater proportion of the *bismuth* is precipitated as a basic sulphate, and the iron is reduced to the ferrous

condition. The liquor is then crystallised, the mother liquors being used for treating a fresh quantity of ore. Copper sulphate is obtained of great purity and in considerable quantity in the refining of silver by precipitating it upon plates of copper from its solution as sulphate (*v.* SILVER).

An electrolytic process for the production of the sulphate consists in using a solution of sodium sulphate and copper electrodes, a current of carbon dioxide being passed through the liquid. Copper is dissolved from the anode as sulphate, while sodium carbonate is produced at the cathode. These react, regenerating sodium sulphate and precipitating copper carbonate, which is collected and dissolved in sulphuric acid (Kroupa, J. Soc. Chem. Ind. 1906, 78).

Palas and Cotta have also described electrolytic processes for the production of the salt (Eng. Pat. 9806, 1899, and 17485, 1900).

The electrolytic production of the sulphate from 'cement copper waters' has been described by Rambaldini (Chem. Zentr. 1909, i. 1675).

It is stated that copper sulphate is sometimes adulterated with ferrous sulphate and Prussian blue to the extent of 90 p.c. (J. Soc. Chem. Ind. 1900, 84).

Copper sulphate crystallises in large transparent blue, doubly oblique rhombic prisms of sp.gr. 2·28, of the formula $CuSO_4.5H_2O$. According to Poggiale, their solubility in 100 parts of water is :

10°C.	20°	30°	40°	50°
36·59	42·31	48·81	56·9	65·83
70°	80°	90°	100°	
94·60	118·0	156·44	203·32	

When heated, it loses 2 molecules of water at 30°, 2 more at 93°–98°, and at 232° becomes anhydrous, white, and hygroscopic, and combines with water with considerable evolution of heat. At 341° the anhydrous salt begins to decompose (Wanjukow, Chem. Zentr. 1909, ii. 1124). The sp.gr. of the anhydrous salt is 3·606 (Thorpe and Watts). It combines with water in alcohol and other organic liquids with production of a blue colour, and may be used for ascertaining the presence of water in those substances, but the test is not delicate. The anhydrous salt is also soluble in *anhydrous* methyl alcohol, and produces a bluish-green solution (Klepl, J. pr. Chem. 1882, 25, 526).

Copper sulphate absorbs hydrogen chloride with evolution of heat, forming cupric chloride and liberating sulphuric acid. It is therefore used to remove hydrogen chloride from such gases as chlorine or carbon monoxide. A similar reaction occurs in solution.

When mixed in solution with molecular proportions of potassium and other sulphates, it produces well-defined, crystalline double sulphates. Several basic sulphates are known.

The sulphate is the most important of the copper salts. It is largely used in calico printing, principally in connection with potassium dichromate or iron mordants; in black dyeing with logwood; directly or indirectly for the preparation of most pigments containing copper; and to prevent rot in timber. In agriculture the crude sulphate containing ferrous sulphate is used to a considerable extent to prevent smut in seeds. The seeds are soaked for some hours in a weak solution of the sulphate, and are sown within 24 hours.

A 10–20 p.c. solution of copper sulphate, preferably mixed with lime, is applied to vines with great benefit. A small quantity is found in the vines and must, but the tannin and sulphur introduced before fermentation appear to remove it in most cases.

Karsten has stated (*v.* J. Soc. Chem. Ind. 1896, 367) that attacks of illness resembling dysentery have been caused by a wine which contained copper in such quantity as to give a visible deposit on steel in 12 hours. Its presence was due to spraying the vines with a copper salt.

An effective wash for vines is prepared by boiling 25 parts of sodium carbonate and 25 parts of resin in 100 parts of water, and then diluting and adding copper sulphate (J. Soc. Chem. Ind. 1899, 155).

Copper sulphate is used in preparing *copper ferrocyanide*, a solution of which, in potassium citrate solution, is used as a toning-bath for photographs (Ferguson's Copper Toning, *ibid.* 1900, 465).

Copper sulphate is also used in dyeing to make diazo- colours permanent to light. The dyed fabric may be treated with the salt (Graebling, *ibid.* 1905, 797), or it may be added to the diazotising bath (Grossmann, Färber-Zeit. 9, 328).

Cupric nitrate $Cu(NO_3)_2$ may be prepared by dissolving copper or the oxide or carbonate in nitric acid. The solution at temperatures above 20° deposits dark-blue crystals containing 3 molecules of water, which melt at 114·5° and boil at 170° with evolution of nitric acid and formation of a green basic salt. This basic salt may also be prepared by boiling the solution of the nitrate with copper or copper hydrate, or with a little alkali (*v.* also *Copper carbonates* for an application of the basic nitrate).

The anhydrous salt may be obtained by the action of nitric anhydride on the hydrated salt. It is a white, deliquescent powder, decomposing at 155°–160° (Guntz and Martin, Bull. Soc. chim. 1909, 5, 1004).

Copper nitrate is used to a slight extent in dyeing and calico printing, and a solution, prepared by mixing solutions of copper sulphate and calcium nitrate, is used in viticulture (Gouthière et Cie and P. Ducancel, Fr. Pat. 395806, 1908).

Cupric sulphide CuS occurs as *covelite* or indigo copper in blue flexible plates, in Vesuvian lava, in Chile, and in the copper-mines of Mansfeld. It may be prepared by heating cuprous sulphide with sulphur at a temperature not above the boiling-point of sulphur; by digesting cuprous sulphide with cold strong nitric acid; or by precipitating a copper solution with sulphuretted hydrogen. On the large scale it is obtained as a paste by precipitating a solution of the sulphate with sodium sulphide. This paste is used in calico printing for the development of aniline black.

The preparation and use of copper sulphide for thermo-couples has been described (Eng. Pat. 11300, 1905).

Rieder has used (Zeitsch. Elektrochem. 1902, 370) an electrolytic method for the preparation of this compound.

A brownish-red *persulphide of copper* has

been obtained by Bodroux by adding a solution of calcium pentasulphide to a solution of copper acetate at 0° (Compt. rend. 130, 1397).

Copper acetate *v. Metallic acetates*, art. ACETIC ACID.

Copper arsenite *v. Scheele's green*, art. ARSENIC.

Cupric phosphate is of no technical interest. A brilliant green colour containing a basic phosphate, prepared by heating a mixture of copper acetate, sodium phosphate, and ammonia, has, however, been used in calico printing (Bourcart, Mon. Sci. [3] 4).

Phosphorus combines in several proportions with copper, and produces true alloys, which in many cases are of great value.

Heyn and Bauer state that the phosphorus exists in the alloy as Cu_3P and Cu_5P_2 (J. Soc. Chem. Ind. 1906, 1047). The latter compound has been obtained by Rubénovitch by the action of phosphine on copper sulphate (Compt. rend. 127, 270).

Copper silicide (*Cuprosilicon*) Cu_4Si is obtained when copper and silicon are heated together in the electric furnace (Vigouroux, Compt. rend. 1896, 122, 318; Lebeau, *ibid.* 1906, 142, 154). It is now manufactured in Germany and America by this process (Steinhart, Eng. and Min. J. 1899, 67, 710), and is used for purifying and hardening copper, and for adding to tin-, zinc-, and aluminium-bronzes to increase their tensile strength and hardness.

Cuprosilicon can be prepared pure by heating together 17 parts silicon and 9 parts copper in hydrogen, and removing the excess of silicon by solution in sodium carbonate. It is silver-white, with a metallic lustre, and is hard and brittle. The sp.gr. is 7·58, and it is attacked by chlorine and *aqua regia* (Vigouroux, Compt. rend. 1906, 142, 87; *see also* Philips, Métallurgie, 1907, 4, 587; and Lebeau, *ibid.* 141, 828).

Copper carbonates. The normal salt has not been prepared, but several basic carbonates are known, and used as blue and green pigments. Basic copper carbonate occurs native as *malachite* $Cu(HO)_2{\cdot}CuCO_3$, and as *azurite* or *chessylite* $Cu(HO)_2{\cdot}2CuCO_3$. When ground, these minerals form a fine but expensive pigment.

An anhydrous basic carbonate is precipitated on addition of a solution of sodium carbonate to a hot solution of copper sulphate or nitrate. (For a complete description of all the known basic carbonates of copper, *see* Pickering, Chem. Soc. Proc. 1909, 188.)

Under the names *Verditer green*, *Verditer blue*, *Bremen green*, and *Bremen blue*, this salt is largely prepared for paper staining &c. According to Habich (Technologiste, 17, 413), the following processes are in use. A hundred parts of old copper sheathing from which impurities, oxide, &c., have been removed by digestion in dilute sulphuric acid, is cut into pieces and mixed with a paste formed by moistening a mixture of 99 parts potassium sulphate and 100 parts common salt, and the mixture is stirred occasionally for some months to ensure thorough exposure to the atmosphere. The action appears to consist in the production of cupric chloride, which, in presence of the metal, becomes converted into a basic chloride, and finally, by the action of the oxygen, into an oxychloride. If the oxidation be incomplete, the subchloride is not completely oxidised, and, as it, when subsequently decomposed by alkali, gives an orange-red precipitate of suboxide, the pigment would be lowered in value. The oxychloride may also be similarly prepared from a mixture of 100 parts copper, 60 parts common salt, and 30 parts strong sulphuric acid diluted with three times its volume of water; or by treatment, with free atmospheric exposure, of copper with a solution of cupric chloride in hydrochloric acid.

To 100 kilos. of this thick magma of oxychloride, which has been washed by decantation, a concentrated solution containing 7 kilos. copper sulphate and 40 kilos. concentrated soda solution (32°–36°Bé.) is added. The mixture is vigorously stirred and poured at once into 150 kilos. of soda solution (20°Bé.). The precipitate is washed, passed through a fine hair sieve, and dried spontaneously or at a temperature below 25°. If hot air be used in the drying, it must be quite free from acid or sulphur gases. To produce the finest colour, desiccation must be perfect.

Habich recommends the following process for making a *verditer* which has a very different composition from the above. A solution of copper oxide in nitric acid is treated with potassium carbonate, which is added in portions until most, but not all, the copper has been precipitated. The green precipitate is washed and introduced into a solution of copper nitrate whereby it is converted into a heavy green insoluble basic nitrate. This is digested in a solution of potassium zincate (formed by dissolving zinc in caustic potash solution). A dark-blue pigment, of great 'body' but little weight, is thus produced. It contains zinc and copper, apparently combined as a double oxide or as 'copper zincate,' and a small quantity of basic copper nitrate.

Verditer may be prepared by agitating a solution of copper nitrate with chalk. The washed pasty precipitate is mixed with 8–10 p.c. of freshly burnt lime with production of a fine velvety blue pigment. The precipitate without addition of lime is green.

According to Gentele, the following process is adopted at Bremen, Cassel, &c.: 225 lbs. sea salt and 222 lbs. blue vitriol, both free from iron, are mixed dry and ground between millstones with water to a thick paste. This paste is mixed in strata with 225 lbs. of clean copperplate cut into pieces about 1 inch square, in wooden chests made without nails, and the mixture is digested for about 3 months with the maximum exposure to air, the whole being well mixed and exposed about once a week. When the action is complete, the undissolved metal is removed and the precipitate is washed with a minimum of water, filtered and thrown into a tub. To 180 lbs. of the magma 12 lbs. of hydrochloric acid (13°Bé.) is added, and the mixture is stirred and left for 24 or 36 hours. Six volumes of this solution is mixed with 15 volumes of caustic alkali (19°Bé.) followed after an interval by 6 volumes of water. The mass is well mixed and left for 36–48 hours, and is then well washed by decantation, filtered, exposed for some time in a moist condition to the air, and finally dried (*v. also Copper monoxide*).

COPPER-GLANCE or **Chalcocite.** Native cuprous sulphide Cu_2S, crystallising in the orthorhombic system. Excellent twinned crystals were formerly found in abundance in the neighbourhood of Redruth in Cornwall (hence the name redruthite) and Bristol in Connecticut; usually, however, the mineral is found as compact masses. It is iron-black with metallic lustre, but, on exposure to light, it soon becomes dull with a powdery black coating. It is soft (H. = 2½) and sectile, and can be readily cut with a knife; sp.gr. 5·7. It occurs in veins of copper ore, and is often of importance as an ore, especially when it contains small amounts of silver. Isomorphous with copper-glance is the mineral *stromeyerite* $(Ag,Cu)_2S$, which has been found in considerable quantities in the Altai Mountains in Siberia. L. J. S.

COPPER PAINT *v.* COPPER.

COPPER-PYRITES or **Chalcopyrite.** A sulphide of copper and iron $CuFeS_2$, containing when pure 34·5 p.c. of copper, and the most important of the ores of copper. It has a characteristic brassy-yellow colour with metallic lustre, and on the surfaces often displays a brilliant iridescent tarnish (peacock-copper-ore). It often occurs together with, and intimately intermixed with, iron-pyrites, from which it can be distinguished by its deeper colour and lower degree of hardness; copper-pyrites (H. 3½–4) is readily scratched with a knife, giving a greenish-black powder, whilst iron pyrites (H. 6–6½) is scratched only with difficulty or not at all. It occurs in mineral-veins and in bedded deposits, and by its alteration gives rise to many secondary copper minerals. Crystals are tetragonal with inclined hemihedrism, but only rarely are they distinctly developed; sp.gr. 4·2. L. J. S.

COPRA and **COPRA OIL** *v.* COCOA-NUT OIL.

COPROLITES. Concretionary mixtures of calcium phosphate and calcium carbonate, derived from the excrements of certain extinct fishes and reptiles. Formerly much used in the manufacture of superphosphate of lime (*v.* FERTILISERS).

CORAL is the calcareous substance secreted by many varieties of five kinds of organisms, viz. (1) *Actinozoa*, the principal constituents of coral reefs; (2) *Hydrozoa*, the large common corals known as millepores; (3) *Bryozoa*, delicate corals in various forms, resembling mosses, branches, thin filamentary deposits, or more solid masses (in the Palæozoic limestone formations this species of coral abounds); (4) *Foraminifera*, chambered shells belonging to lowly organisms, mostly of very minute size; (5) *Nullipores*, which, although closely resembling millepores, are veritable algæ or sea-weeds; they may be readily distinguished from the millepores by the absence of perforations.

Coral is simply a secretion corresponding to the bone of vertebrates or the shell of mollusca, and is composed almost entirely of calcium carbonate derived from sea-water and from the food of the coral-making polyps.

Ordinary coral is somewhat harder than limestone or marble, and, when tapped with the hammer, gives out a ringing sound clearer than is elicited from ordinary calcium carbonate. The sp.gr. of 15 specimens examined by Silliman, averaged 2·523.

COMPOSITION OF CORAL.

S. P. Sharples (Amer. J. Sci. 31, 168) found

—	Calcium carbonate	Calcium phosphate	Water and organic matter
Oculina arbuscula, N. Carolina	95·37	0·84	3·79
Manicina areolata, Florida	96·54	0·50	2·96
Agaricia agaricites, Florida	97·73	0·53	1·64
Siderastræa radians, Florida	97·30	0·28	2·42
Madrepora cervicornis, Florida	98·07	0·32	1·93
Madrepora palmata, Florida	97·19	0·78	2·81

Small and variable quantities of magnesium carbonate, calcium sulphate, calcium fluoride, alkaline chlorides, silica, and oxide of iron are found in corals.

The red coral, *Corallium rubrum*, varies in colour from crimson to rose, the latter being the rarest and, therefore, the most prized. It is gathered from the rocky bottom and shores of the Mediterranean; and it occurs most abundantly at a depth of 25–50 feet; although, according to Dana, it may be found as deep as 1000 feet. Forchhammer found 2·1 p.c. magnesia in *Corallium rubrum*, and 6·36 in *Isis hippuris*. According to Trommsdorff, the red pigment of coral is a resin soluble in oil of turpentine, and, after removal from the coral by this solvent, is easily soluble in alcohol and ether, but insoluble in caustic potash. In a red madrepore, Vauquelin found a red colouring matter, which was turned violet by alkalis. Moseley has described in some corals and allied organisms a red colouring matter (*Polyporphyrin*) which is insoluble in water, glycerol, alcohol, ether, and in strong solutions of ammonia and potash. It is soluble in moderately strong sulphuric, nitric, or hydrochloric acids. For the formation and distribution of coral and coral-reefs, &c. *v.* Corals and Coral Islands, J. D. Dana; Coral-Reefs, Darwin; Murray, in Proc. Roy. Soc. Edinb. 1880, 505. *See also* Forchhammer, J. Pharm. Chim. 49, 52; J. 1847, 1291; 1849, 813; 1851, 865; 1852, 958–961; Sharples, *l.c.*; Moseley, Quart. Journ. Microscop. Sci. xvii. 1877; also Max Bauer, Edelsteinkunde, 2nd ed. 1909, Eng. trans. Precious Stones, L. J. Spencer, 1904.

It is now known that the materials constituting coral-reefs sometimes undergo remarkable chemical changes, and that the calcium carbonate is largely replaced by magnesium carbonate or calcium phosphate. In 1846 J. D. Dana and B. Silliman showed that the rock of an upraised coral-reef in the Pacific contained as much as 38 p.c. of magnesium carbonate. The deep boring made in the Atoll of Funafuti in 1897–8, yielded a series of cores, of which a chemical examination was made by E. W. Skeats and Hart Smith in the laboratories of the Royal College of Science. It was found that down to the depth of

637 feet dolomitization had only gone on to a small extent, the proportion of magnesium carbonate never exceeding 16 p.c.; but the lower portions of the core were very rich in the magnesium salt, containing from 30 to 43 p.c., the rock thus becoming almost a true dolomite. A large collection of coral limestones obtained by Alex. Agassiz, from reefs in the Pacific, was subsequently examined by Skeats, who showed that they contained varying amounts of magnesium carbonate up to nearly 42 p.c. Specimens from Christmas Island in the Indian Ocean gave similar varying results, per centages of magnesium carbonate up to over 43 p.c. being found. A coral limestone obtained by boring at Key West, Florida, yielded to G. Stieger, in the laboratories of the U.S. Geological Survey, over 14 p.c. of magnesium carbonate.

Coral reefs that have been covered by deposits of guano are found to have their carbonates largely replaced by phosphates. Thus the rocks of the coral reef known as Christmas Island in the Indian Ocean have been largely worked for the deposits of calcium phosphate, and Teall has shown that Clipperton Atoll in the North Pacific contains rocks with as much as 38½ p.c. of phosphoric acid.

(For changes in the chemical composition of coral rock, *see* Dana and Silliman, Amer. J. Sci. 2, i. 1846, 189; Judd, Chemical Examination of Materials from Funafuti in 'the Atoll of Funafuti,' Phil. Trans. 1904, 362–389; Skeat, The Chemical Composition of Limestones from Upraised Coral Islands, Bull. Mus. Comp. Zool. Harvard, xlii. 1903, 53–126; Teall, Quart. Journ. Geol. Soc. liv. 1898, 230–232.)

CORALLIN, CORALLINPHTHALIN, PHENOLCORALLIN *v.* AURIN.

CORDIALS and **LIQUEURS** are spirituous compounds flavoured with essences obtained from fruits, herbs, spices, or other substances, usually sweetened with sugar or glycerol, and often strongly coloured. They are manufactured and used to a much greater extent in France and other European countries than in the United Kingdom, and although there is no essential difference between them, the term 'cordials' is by many restricted to British, and 'liqueurs' to the foreign preparations.

The spirit in the best qualities of liqueur is derived from the grape, but grain and other spirit is frequently employed, especially in cordials; but, whatever the origin of the spirit, it should be highly rectified and neutral in character, so as not to impair the flavour of the finished product. The alcoholic strength of cordials and liqueurs varies greatly, but, on the average, they contain from 30 to 40 p.c. of alcohol, or 50 to 70 p.c. of proof spirit. The sugar must be pure, and is added in the form of a clear syrup.

The principal flavouring ingredients employed are (*a*) those used solely on account of their essential oils, as aniseed, bitter almonds, caraway, juniper berries, mint, lemon peel, orange blossom, &c.; (*b*) those valued for their bitter principles as well as their essential oils, as cinnamon, cloves, curaçoa apples (a kind of orange), gentian, ginger, orange-peel, sweet calamus, wormwood, vanilla, &c.; and (*c*) fruits, chiefly cherries, pineapples, raspberries, and strawberries. The flavourings are obtained either by digesting the flavouring ingredients (bruised or cut up) with alcohol and distilling the mixture to obtain an essence, or by filtering the alcoholic extract to form a tincture, or by simply expressing and clearing the juice of fruits or digesting the latter for a more or less prolonged period in spirit.

Artificial essences simulating the above flavourings are frequently employed, but their use in beverages is questionable, since it seems probable that their physiological action differs from that of the natural flavouring substances which they are intended to imitate.

The colouring matters most commonly used are as follows. *Red*, aniline red, brazilwood, cochineal, cudbear, and sandalwood; *yellow*, saffron and turmeric; *blue*, indigo; *green*, chlorophyll (from nettles, parsley, spinach, &c.) and mixtures of blue and yellow colourings; *violet*, aniline violet; and *brown*, a solution of burnt sugar or caramel (*v.* LIQUEURS).

J. C.

CORDITE *v.* EXPLOSIVES.

COREINE *v.* OXAZINE COLOURING MATTERS.

CORIANDER, OIL OF, *v.* OILS, ESSENTIAL.

CORIARIA MYRTIFOLIA *v.* SUMACH.

CORIOFLAVINE *v.* ACRIDINE DYESTUFFS.

CORIOPHOSPHINES *v.* ACRIDINE DYESTUFFS.

CORK. Cork is derived from the bark of two evergreen species of oak tree, the cork oak, *Quercus suber* (Linn.) and *Q. occidentalis* (Gay). The former yields the best cork, and grows mostly in those countries bordering on the Mediterranean up to the 45° lat. The latter occurs on the Atlantic seaboard of Portugal, Spain, and France up to 48° lat.

The cork tree is from 30 to 60 feet high, and 3–4 feet thick. It grows slowly and reaches the age of 150–200 years. The tree has the peculiarity of throwing off its outer bark when it reaches a certain age, and then reproducing it. It is this that makes the cork industry possible. The chief countries in which cork is produced are:

1. *Spain.* Particularly the province of Catalonia. Here the best cork is grown. Seville is the chief market.

2. *Portugal.* Centres: Lisbon and Oporto.

3. *Algeria.* Here the cork trees form great forests; those belonging to the State were some years ago fully 600,000 acres in extent.

4. *Southern France* and the *Pyrenean district.* Large forests of *Q. suber* exist in the more mountainous parts, but in the low-lying 'Landes' the tree is *Q. occidentalis*, which grows as far north as Belle Isle.

5. *The Adriatic coast.* Some is produced in the Austrian provinces, but it is of inferior quality.

6. *Sicily*, *Sardinia*, and *Corsica* also yield cork of good quality.

Speaking generally, the cork tree seems to thrive best on dry granitic and sandy soils, and not to do well in damp or limestone soils.

The complete bark of the cork tree consists of two layers:

(1) The dry dead bark, comprising the epidermis and the cork proper, with the mesodermis.

(2) The green living skin which clothes the wood immediately under the dry bark. This may be looked upon as the active cork-producing

layer, and contains bast fibres and the endodermis.

The epidermis on one-year-old twigs is green and smooth, but in the second year between it and the green under-skin irregular white waxy masses are formed; these represent the beginning of the cork formation and increase from year to year, changing gradually into cork proper. At the end of the third year the epidermis dries up and cracks.

Barking the trees. This is the most important operation in the management of a cork forest, because on the care with which it is carried out depends the life of the trees and the regularity of the slabs produced.

In barking, the workman takes a special tool and makes a cut round the stem above and below the portion of bark to be removed. A vertical cut or cuts are made so that the bark may be stripped off the tree, in which operation the shaft of the tool is used as a lever. Care must be taken not to bruise the green underskin, the real producer of the cork.

The first barking produces so-called 'virgin cork,' which is of little value, as it has not elasticity enough for use as bottle corks. It was formerly used for the production of Spanish black, but of late years it has been employed in the manufacture of ground cork.

During the first year of growth the tree produces from 3 to 5 mm. of cork, but afterwards less, the mean for the first 9 years being about 2·1–3 mm., giving a total thickness of 20¾ mm. After 9 or 10 years, when barking usually occurs, the growth is slower, but where thicker cork is required, the period is of course longer. The first stripping usually takes place on the 15–20 year-old tree. The best cork is yielded by trees of from 50 to 100 years old. Those growing in the mountainous districts yield a smaller quantity but better quality of cork.

After the cork bark has been removed from the tree, it is stacked and weighted with heavy stones to flatten it, and when dry it is scraped with an iron tool to remove the epidermis. The cork is then immersed for 5 or 6 minutes in a tank of boiling water, when it swells, and, according to the quality, retains this swelling more or less permanently. The water also removes tannin, vegetable acids, and their salts. In Spain the cork is occasionally passed through a fire, whereby it is superficially blackened, acquiring, it is supposed, by this treatment especially good qualities or 'nerve.'

After steeping, the plates are placed in heaps, weighted, and by hydraulic presses compressed into bales and bound with hoop iron.

Chemistry of cork. Cork extracted with hot water under pressure, yields gallic acid, colouring matters, iron and magnesium salts. By extraction with alcohol it yields 'cerin,' or cork wax $C_{32}H_{20}O$. Siewert examined the alcoholic extract and isolated from it 'decacrylic acid' $C_{10}H_{18}O_2$.

The composition of cork has been further studied by Kügler (Arch. Pharm. 1884, 217); Gilson (*ibid.* 1890, 690); and Hy. Ingle (J. Soc. Chem. Ind. 1904, 1197).

Suberine, according to Kügler, is a real fat, which cannot be entirely extracted by solvents, because they do not penetrate the material sufficiently.

Gilson saponified cork from *Q. suber* with 3 p.c. alcoholic potash, and isolated from the filtrate 44 p.c. of fatty acids, consisting of: *Phellonic acid* $C_{22}H_{32}O_2$, m.p. 95°–96°, a monobasic acid giving a violet colour with zinc chloride-iodine solution; yield 8 p.c. *Suberinic acid* $C_{17}H_{30}O_3$, a semi-fluid sticky substance; 36 p.c. *Phloionic acid* $C_{22}H_{40}O_7$: fine white needles, m.p. 120°–121°; in small amount.

Gilson considers suberine not to be a true fat, but rather a mixture of complex esters and possibly condensation products of different acids.

Treated with iodine solutions cork does not give the cellulose reaction, and there is some dispute as to whether cellulose or a pentosan is the carbohydrate present in cork. Gilson, from microscopic examination, considers that cellulose is present.

Cork also contains certain aromatic compounds, tannin and the aromatic aldehyde of wood, hadromal, besides coniferin and vanillin.

Treated with strong nitric acid, cork produces suberic acid $(CH_2)_6(COOH)_2$, oxalic acid, and other products. Strong sulphuric acid chars it, but it is little affected by hydrochloric acid. Chlorine, bromine, and iodine cause cork to shrink, the two former first bleaching it. Ignited it burns, swells up, and forms a charcoal called Spanish black.

Physical properties.—The sp.gr. of cork is variously given from 0·12 (Rollmann) to 0·24 (Muschenbroek); on the average 0·16.

The uses of cork depend on its compressibility, elasticity, imperviousness to liquids, its lightness, its stability to weathering, &c. It is used in making stoppers, mats, soles, linings, springs for heavy waggons, as anti-vibratory and sound-deadening materials.

Waste cork is granulated by suitable machinery, sifted, and then ground to powder. The finest dust is mainly used in the manufacture of linoleum. Slightly coarser cork is used for the manufacture of cork carpet, but in both cases the binding material is prepared linseed oil.

Still coarser cork, of the size of peas, mixed with a proportion of fine, is employed in the manufacture of mats, insulating materials for water and steam pipes and cold storage chambers, packing, artificial corks for bottles, &c.

In order to bind the particles of cork together are employed (1) collodion; used for bath mats and stoppers. The granulated cork of various grades in suitable proportions is mixed with the solution and the pasty mass pressed into perforated moulds; these are then heated in a suitable chamber provided with a condensing appliance to recover the solvents, ether and alcohol. 'Suberite' belongs to this class. The mat is removed from the mould and 'buffed' (sand-papered) on a buffing machine similar to that used by cabinet makers. Cork stoppers are made in a similar manner, and also insulating slabs and tubes for covering steam and water pipes.

(2) Gluten, casein, and glue mixed with oily materials and resins and dissolved in suitable solvents, after mixing with the cork (rendered more or less insoluble by means of formalin, tannin, dichromates, lime, &c.), have also been used and patented for the production of cork slabs, &c., from granulated cork. The cork of various degrees of fineness is

mixed with the cement, subjected to powerful hydraulic pressure in moulds, and in some cases heated up to 200° to harden the albuminous matters of the cement.

(3) Mixtures of cork with silicate of soda and barytes or other pigment have been used for steam-pipe coverings.

Slabs of cork have also been made by soaking cork in soap solutions, then drying, treating with milk of lime, again drying and pressing the resultant mass into heated moulds.

Another use for cork waste, more or less finely ground, is in the production of floors. In this operation ground cork is mixed with a cement, such as Portland cement, or more often a mixture of cork and calcined magnesia is mixed with a solution of magnesium chloride and the pasty mass spread on the floor and allowed to harden; other salts, such as lead acetate, are sometimes added.

Cork dust is also used as a packing for the hollow spaces between the walls of cold-storage chambers, round the pipes of ice plants, &c., no binding materials being employed. Mixed with pitch, granulated cork is used as the filling between the outer and inner soles of boots, especially American. It forms a warm, waterproof and resilient layer.

Granulated cork of various degrees of fineness is also mixed with the paint used to coat iron surfaces where there is danger of the condensation of moisture, such as in the cabins of steamers, in breweries, factories, laundries, and the like.

Hy. I.

CORNISH CLAY *v.* CLAY.

CORNISH STONE *v.* CLAY and CHINA STONE.

CORN OIL *v.* MAIZE OIL.

CORNUTINE *v.* ERGOT OF RYE.

CORONITE. An explosive consisting of nitroglycerine, 38–40 parts; nitro-cotton, 1–1½ parts; ammonium nitrate, 26–28 parts; potassium nitrate, 3–5 parts; aluminium stearate, 11–14 parts; rye flour, 8–11 parts; wood meal, 2–4 parts; liquid paraffin, 2–4 parts (*v.* EXPLOSIVES).

CORROSION OF IRON. All forms of metallic corrosion are probably primarily due to electrolytic action, and if it were possible to obtain absolutely pure iron, it might be found to be as resistant to atmospheric action as pure zinc is to dilute sulphuric acid; but with cast or wrought iron and steel, protection from air, moisture, and carbon dioxide is a necessity if the metallic form is to be preserved.

Iron rust, the result of atmospheric action under normal conditions, consists mainly of a mixture of ferric oxide Fe_2O_3, and ferric hydroxide $Fe_2(HO)_6$, but a sample of fresh iron rust will be found to contain, in addition, ferrous oxide and ferrous carbonate. These two compounds, however, soon become oxidised, the latter setting free carbon dioxide and forming ferric oxide.

If a piece of iron be immersed in pure water, no action will be found to have taken place even after the lapse of some time, the presence of oxygen or air, which, however, must be quite free from any trace of carbon dioxide, in no way affecting the result; but the moment any carbon dioxide finds its way into solution in the water, rusting rapidly commences, and hence it is clear that the carbon dioxide dissolved in the water and forming carbonic acid is the prime factor in starting the corrosion of iron and steel.

When iron or steel is acted upon by water free from any dissolved oxygen, but saturated with carbon dioxide, ferrous carbonate is formed, together with free hydrogen:

Iron	Carbonic acid	Ferrous carbonate	Hydrogen
Fe	$+ H_2CO_3 =$	$FeCO_3$	$+ H_2.$

The solution remains clear, the salt being soluble in the excess of carbon dioxide present, until it is exposed to air, when the oxygen oxidises the ferrous carbonate to ferric oxide, setting free the carbon dioxide.

Ferrous carbonate	Oxygen	Ferric oxide	Carbon dioxide
$4(FeCO_3)$	$+ O_2 =$	$2(Fe_2O_3)$	$+ 4CO_2.$

The ferric oxide then combines with some of the water to form ferric hydroxide:

Ferric oxide	Water	Ferric hydroxide
Fe_2O_3	$+ 3H_2O =$	$Fe_2(HO)_6.$

The carbon dioxide which is set free then reacts with more of the oxygen and moisture to attack a fresh portion of the metal, the action, moreover, being aided by the electrical difference in potential between the hydrated oxide and the metal, so the result is that in time the whole of the metal is destroyed by its reversion to its original condition of hydrated oxide.

In large towns considerable quantities of sulphur acids are found in the atmosphere, owing to the combustion of bituminous coal, which, containing a small percentage of iron pyrites, leads to the formation of sulphur dioxide, and this dissolving in rain rapidly oxidises to sulphuric acid, giving the rain water an acid reaction. It has been shown that in the industrial quarters of a large manufacturing town this acidity will sometimes represent as much as 90 lbs. of sulphuric acid per acre per annum, whilst in the residential quarters it will probably not be more than about 25 lbs. The sulphuric acid, however dilute, coming in contact with ironwork, accelerates the rusting, and by its corrosive action renders more difficult the protection of the metal.

The usual methods of protecting iron and steel from atmospheric corrosion may be divided roughly into two classes; the first consists in coating them with another metal less liable to be acted on than the iron, and the second in the use of protective paints. Under the first category comes the coating of iron and steel by zinc, as in the process of galvanising; with tin, as in the manufacture of tin plate, whilst for small articles nickelling and also protecting by the Bower-Barff process, in which the iron is coated with a homogeneous film of the magnetic oxide, may be used. In the case of zinc, this metal, being electro-positive to the iron, forms a good protection until acid in the atmosphere or abrasion damages the surface, when, forming a galvanic couple with the iron, it is rapidly destroyed. The other coatings are all electro-negative to the iron, with the result that any break in the coating leads to far more rapid destruction of the iron than if none had been present. For the protection of large structures, coating with paint of suitable composition is the only practicable method of rust prevention.

The best paints for this purpose consist of

boiled linseed oil mixed with suitable pigments. When linseed oil is heated for some hours to about 200°, its oxygen-absorbing properties, upon which its drying depends, are very largely increased, and if it be boiled with oxides of lead, calcium, or manganese, the drying action is still further accelerated, owing to the formation of small quantities of oleates of the metals which dissolve in the oil. On exposing the boiled oil to air, oxygen is rapidly absorbed, and drying is brought about by the conversion of the liquid oil into a solid resin. If white lead (oxycarbonate of lead) or red lead (an oxide) be thoroughly ground in such oil, a paint is formed which has great covering power, and which, in air, forms the best protection the iron can have, as microscopic examination shows that the dry film of paint contains no pores, and so forms an impervious coating.

The covering power and impervious nature of such a paint are due to the fact that the lead compound has formed with it a soap (oleate of lead), whilst in most other pigments no such combination takes place, and the particles of colour are merely mechanically carried by the vehicle.

Such paint will resist atmospheric influence for a long time, but eventually the protecting skin becomes hardened and brittle, so as to be easily chipped off, whilst as the decomposition proceeds still further, it loses all its adhesive powers and flakes off from the metal. Red oxide of iron free from foreign matters and any trace of acid also forms a good pigmentary material for a protective paint, and is especially popular with paint manufacturers, as its colour masks any rusting that may go on below it.

Many cheap paints of this character, however, prove unsatisfactory, owing to the oxide of iron being largely adulterated with finely powdered barium sulphate, which, being very heavy, is often used as a 'loading.'

The best treatment for large iron structures is, in the first place, to entirely free them from all traces of 'bloom' or mill scale which may be adhering to them, this being done either by pickling in dilute sulphuric acid with subsequent neutralisation of the acid, which should be done before erection, or by allowing them to flake off by the formation of a film of rust from exposure, and then wire-brushing the surface until it is free from any trace of oxide.

The surface so prepared should, at the time of painting, be thoroughly dry, and under these conditions a coating of hot linseed oil, followed by two coats of red lead paint, and finished off with two coats of iron oxide paint, will give the best protection that can be obtained.

Varnish paints, such as will be described later, for use in coating ships, are not to be recommended for outside work, as under atmospheric influences they often tend to become brittle.

Almost equally good as the red or white lead paints as a protection is a bituminous paint made from pitch, the distillation of which has not been carried too far. This must be absolutely free from free carbon and tar acids or ammonium salts, and if applied hot to the structure to be protected, gives very good results, the colour being the main drawback.

There are many circumstances under which such a bituminous paint is preferable to an oil paint, as, for instance, in gas works, urinals, or slaughter houses, where there is much ammonia in the air, which has an extraordinarily destructive effect upon oil paints.

In the manufacture of paints for protective purposes it is essential that the materials should be ground to the utmost degree of fineness, and great attention should be paid to the thorough incorporation of the pigment with the vehicle, whilst where several coats of paint have to be superimposed on each other, the composition should be so arranged that the rate of drying of each coat should be a little less than the one below, as this prevents any chance of the upper film hardening before the lower coating, which would result in cracking the coating of paint. It must also be borne in mind that in painting an iron structure, the skin left by the paint should have the same rate of expansion and contraction as the metal, or be sufficiently elastic to prevent any cracking away from it.

In cases where rusting begins to show itself by the blistering and upheaval of the paint surface, the plating at that point should be scraped down to the bare iron, and well scrubbed with a wire brush in order to remove the traces of foreign matter that are probably giving rise to rapid corrosion due to electrolysis.

V. B. L.

CORROSION AND FOULING OF STEEL AND IRON SHIPS, AND ITS PREVENTION. In the days of wooden ships the hull troubles that had to be guarded against were the attacks of wood-boring animals and the loss of speed due to the growth of weed and shell at and below the water line; but with the launch of the first sea-going vessel built of iron, in 1822, comparatively simple problems became of great complexity, and at the present time the protection of our Navy and mercantile marine from corrosion and fouling is a question of the greatest importance, affecting, as it does, both the life and speed of the vessels.

Corrosion.—The troubles due to corrosion are by no means limited to the exterior plates of the ship, but also affect the interior of the structure, boilers, and condensers.

The corrosion of iron and steel is brought about by the actions which ultimately result in the conversion of the metal into oxides, and these being accelerated by galvanic actions, which it is almost impossible to eliminate in a huge metallic structure like the hull of a modern ship in the presence of sea water, makes prevention far more difficult than in the case of an iron building or bridge.

In sea water the process of corrosion is accelerated by the salts contained therein, as these aid the galvanic action set up in the metal by various means, such as impurities in the iron, the presence of mill scale on the plates, high temperature, or even the different stresses imparted to portions of the same plate, whilst in certain waters, such as the mouths of rivers on the west coast of Africa, or in harbours where the water contains much sewage, the sulphates are decomposed by various vegetable and animal organisms with evolution of sulphuretted hydrogen, which greatly increases the corrosion of the metal.

The examination of the condition of the

bottom plates of vessels that have been at sea for long periods, shows, when the protective paints and compositions have been removed, that three distinct forms of rusting may be distinguished.

1. Rust patches, generally near the edges of the plates, consisting of small areas of fine rust, probably caused by moisture on the plate when the protective paint was put on. These patches are never thick, and cause but little damage to the plates if all rust be removed before a new coating of paint is put on.

2. Rust nodules are a more localised form of corrosion which has attacked the metal where particles of mill scale have been left on the surface of the new plate, or where small particles of slag or foreign matter have been rolled into the plate during manufacture. These give slight pitting of the plate, but seldom to a serious extent.

3. Rust cones are an accentuated form of rust nodules, and are due to the most local form of galvanic action, caused by the presence of a speck of deposited copper, lead, or other foreign metal, or even a small particle of rust or mill scale left on the surface of the iron, and covered by the compositions used as protectives and antifoulers. As soon as the sea water penetrates these, galvanic action is set up, water is decomposed, rust formed, and the escaping hydrogen pushes up the composition, forming a blister; the hydrogen escapes and water leaks in, the action becoming more and more rapid, and the blister gradually filling with the product of the action—rust. The blister bursts, but the cone of rust has by this time set fairly hard, and continues to grow from the base, the layers of rust being easily distinguished in a well-formed cone, and when the rust cone is detached, the pitting of the metal at the base of the cone is, as a rule, found to be of considerable depth.

Extensive researches by Andrews, Phillips, and others show that, as a general rule, steel corrodes more quickly than iron in sea water, and that the rate of corrosion increases very rapidly with the length of exposure, owing to the galvanic action exerting a greater influence as the amount of oxide increases; but with the almost universal adoption of mild steel as the material for the construction of the hulls of modern ships, this trouble has not proved as serious as was at first feared would be the case.

Certain portions of a ship's hull are exposed to special risk of corrosion from galvanic action, owing to the bearings of the screw shaft and valves for the escape of waste water, bilge, &c., being made of alloys containing copper. In order to prevent this, zinc protectors, consisting of heavy masses of the metal, are placed round all openings where copper or copper alloys are present, and the zinc, being more electro-positive than the iron, places the iron in the electro-negative condition, so that whilst the iron escapes injury the zinc rapidly dissolves.

Protection of iron from corrosion.—In order to protect the outer surface of iron and steel structures, two different methods have been tried. The first process is to coat the iron with another metal which is less liable to be attacked by the moist carbon dioxide and oxygen, or which is electro-positive to iron, whilst the second is to cover it with some paint or varnish which will prevent these harmful compounds from acting on it.

The chief metals which have been tried for coating the iron are zinc, tin, nickel, and copper. Of these zinc has been very extensively used, and the galvanising of the thin plates used in many forms of craft proved a very valuable protection, but the sheathing of vessels with zinc, which has also been tried, never proved very successful. With the other metals, as long as the iron is protected by the coating remaining intact, no corrosion will result, but as soon as the surface of the metal becomes abraded, the iron will rust at a much greater rate than if it had been left unprotected, as the two metals will set up a galvanic current, in which the iron is the electro-positive element, which vastly increases the corrosive effect, and at the present time this class of protection has practically been abandoned for ships.

The second method of protecting the exterior of the bottoms of iron and steel ships from corrosion, and which is the one most universally adopted, is to coat them with so-called anti-corrosive or protective paints and varnishes. In order that this should be successful, much depends upon the state of the hull at the time at which the protective is put on.

The bottom plates of the newly built vessel are thickly coated, as a rule, with mill scale or magnetic oxide of iron Fe_3O_4, which is formed on the surface of the plate during rolling, and which, if it remains perfectly intact, would be an excellent protective, as it forms, indeed, the basis of the Bower-Barff process for the protection of iron; but during the shearing and rivetting of the plates this scale gets broken off and exists only in patches, which, if left upon the plate, would excite rapid local galvanic action, owing to the fact that this scale is strongly electro-negative to the iron, so that it would need only the exciting influence of the sea water to start the action.

In naval vessels, the plates are pickled in dilute sulphuric acid until all the scale is removed, and all traces of the acid are in turn destroyed by immersing the plate in lime water or other alkaline solution, a precaution which is extremely necessary, as, if any trace of iron sulphate is left on the plate, this again is actively corrosive.

In the mercantile marine it is an ordinary practice to launch a vessel without any paint on the hull, leaving the active, but fairly even, rusting which ensues to remove the scale, the ship being scrubbed down and then protective compositions painted on when it is docked.

This method has the advantage of cheapness, and also of giving a very slightly roughened surface, to which the protective composition adheres firmly, and answers well with tramp steamers and other craft where speed is not an object of paramount importance; but with service vessels and liners, slight as the roughening is, it undoubtedly has an influence on the speed.

The hull of the vessel, being perfectly free from mill scale, and as free as it can possibly be got from the ordinary oxide, is then painted with the protective, but for this to prove effective, the hull must be absolutely dry, a condition which it is exceedingly difficult to obtain, as the big mass of iron is generally a few degrees

in temperature below that of the moisture-laden air, and under these conditions a trace of moisture condenses on the surface, which is spoken of as 'sweating' of the metal, and this prevents the proper adhesion of the paint to the metallic surface, and also starts rusting under the paint.

With electricity available for utilisation in an air heater, it would, in most cases, pay to dry the hull with a hot-air blast, while the first coat of protective is being put on.

The anti-corrosion or protective paints used for coating ships' bottoms may be classified as:

1. Oil paints.
2. Heavy hydrocarbons. such as pitch, asphalt, or tar.
3. Varnishes, resins, and gums dissolved in volatile solvents.
4. Varnish paints, containing metallic oxides to give them body.

Oil paints are the oldest form of protectives in use, and, when the plates are painted when hot and dry, amongst the best and most lasting; but the drying of such paints, being dependent upon the slow oxidation of the boiled oil by air into a resin, requires that a considerable time must elapse between the painting of the ship and the coating becoming hard enough to allow of the anti-fouling composition being painted on over it, and as a rule so short a time is allowed for docking that this is a great drawback.

The old paints for this class of work used to consist of red or white lead mixed with boiled linseed oil, but it was shown by M. Jouvin that with the perishing of the vehicle the lead compounds were converted into chlorides and oxychlorides by the sea water, and these were then reduced by the action of the iron of the hull with formation of crystals of lead, which set up galvanic action and led to rapid corrosion.

A ship before her launch often receives a coating of such paint from the builder, which is generally scraped off before she is finally coated for service with her protective and anti-fouling compositions.

Undoubtedly the best and most lasting protectives belong to the second class, and a good pitch containing little or no free carbon, or an asphalt painted on when liquefied by heat, gives perfect protection to the metal below it. Unfortunately, the pitch and tar made at the present time are unfitted for such work, as the high temperature employed in gas making has ruined the quality of the tar, which often contains over 30 p.c. of free carbon and naphthalene.

In case tar or tar products are used, care must be taken to free them from all traces of tar acids or ammonium salts, both of which tend to increase corrosion.

The third and fourth classes of protectives came into use when it became necessary to cut down the time expended in docking, and they owe their rapid drying powers to the fact that, instead of waiting for oxidation to form a resinous mass, as in the drying of boiled oil, a resin is dissolved in a highly volatile solvent, being mixed with boiled linseed oil to give the necessary elasticity, and when this is painted on the hull of the vessel, the rapid evaporation of the solvent leaves the resin and oxidised oil binding the body colour together.

Shellac, rosin, kauri, and many other gums and resins are used, whilst the solvents may consist of light hydrocarbons, such as the various grades of solvent naphtha, alcohol, and even fusel oil, but in the Navy very low flash-point solvents have now been discarded owing to the danger in storage.

In most of the various paints red oxide of iron is used to give body and colour to the mixture, and, as it is the same colour as the rust that may form under it, it is very popular with the composition manufacturer, and, providing it be free from acid and soluble sulphates, is unobjectionable; but perhaps a better material would be the mixture of finely divided zinc and zinc oxide, such as is obtained in the Belgian process of distilling zinc, as, even after the varnish had perished, the zinc would afford a further term of protection.

The drawbacks to the last two classes of protectives are that the solvents employed for dissolving resins and gums are mostly affected by water, with the result that if the plates are not dry, the resins are apt to be deposited in a pulverulent condition, whilst the cold produced by the rapid evaporation of the solvent tends to increase the amount of moisture deposited, which assists in the deterioration of the coating.

These varnishes also, even when dry, are not impervious to gases and liquids. Under a microscope the coating is seen to be full of minute tubes, through which the sea water finds its way to the iron beneath, and, when once corrosion has been started, the protective coating is gradually forced away from the surface of the iron, exposing more metal to be acted upon. The best results are secured by employing several coats of the varnish, and applying it only in weather favourable to the operation, plenty of time being given for the thorough hardening of the material before water comes in contact with it.

The protection of the interior surface of the hold of a ship presents some special complexities, as it is exposed to the wear and tear of taking in and discharging cargo, and one has to take into consideration such sources of trouble as the action of bilge water, the high temperature, and the presence of foreign bodies such as coal-dust and leakages from cargo. There are three classes of protectives used for the interior portion of a ship:

Cements;
Bituminous coatings;
Paints.

Although cement is very largely used, yet there are certain drawbacks attached to it which render it by no means the ideal material. It has a certain amount of porosity, so that any corrosive liquid penetrates it and acts on the iron beneath; its rigidity causes it to come away from the metal on any strain being thrown on the latter, variations in temperature having the same effect, and where the coating has parted from the iron, corrosion will start and remain unseen until perhaps too late.

Bituminous coatings applied hot are far preferable to cement, but are rather more troublesome to put on.

Corrosion of boilers.—A serious form of corrosion is to be found in the rusting and pitting of the plates and tubes of high-pressure

boilers. Before the adoption of mineral lubricants, it was supposed that the decomposition of the lubricating oils by the superheated steam in the cylinders caused the corrosion owing to the fatty acids liberated, but the same effect has been found with hydrocarbon oils, so that the pitting is evidently not due to this cause.

There are several causes which lead to the corrosion found in boilers, amongst which are ordinary corrosion, set up by the carbon dioxide and oxygen which occur naturally in all water, and which act on the metal when the boiler is out of use. This form of corrosion can be prevented by filling the boiler quite full with boiled water rendered slightly alkaline with a little lime and closing air-tight whilst at rest. Secondly, galvanic action, induced by the difference in potential between the rust formed by ordinary corrosion and the iron, and also by metallic impurities in the iron and specks of foreign metals deposited upon it. This action can be prevented to a great extent by the use of zinc blocks inside the boiler and in metallic connection with the iron of the plates. A third cause of corrosion is to be found in the solvent action of distilled water upon the metal of the boiler, the action getting less with increase in the quantity of salts in solution in the water. The fourth cause arises from the high local temperature brought about by incrustation or deposits on the surface of the tubes or plates; at such places the temperature often is not far below that of a dull red heat, and then iron is able to decompose water, forming black magnetic oxide of iron and liberating hydrogen:

$$4H_2O+3Fe = Fe_3O_4+4H_2.$$

The obvious remedy for this trouble is, of course, to prevent the formation of incrustation by paying attention to the water with which the boiler is fed, and with the use of 'softened water' or condenser water, which has been passed through an oil filter, the trouble disappears.

Corrosion of condenser tubes.—Alloys of copper and zinc in certain proportions, when subjected to the corrosive action of sea water and carbon dioxide, gradually lose the zinc from the alloy, and this leads to serious pitting, and corrosion, especially in the case of condenser tubes, which are made of copper-zinc alloys, and are exposed to the action of sea water used for cooling on one surface and to the solvent action of distilled water on the other.

It has been found, however, that the addition of 1 p.c. of tin to a brass containing at least 70 p.c. of copper practically puts an end to the trouble. Even where a good brass has been used for the condenser tubes, it is occasionally found that corrosion takes place, but the cause is probably the presence of some foreign material or want of uniformity in the composition. Bronze does not corrode readily when in contact with iron, but is slowly attacked when associated with copper.

Fouling of ships and its prevention. The question of the fouling of ships' bottoms is one that has existed from the earliest days, and was, indeed, of even more importance 200 years ago than it is at the present time, owing to the increase in dock accommodation allowing the more frequent cleaning and painting of the ships; but even now in the case of war the loss in speed during blockading operations, owing to the fouling of the vessels, might prove an important factor in a struggle for supremacy.

Fouling consists of various marine growths, both animal and vegetable, which attach themselves to the bottom of the vessel, and by increasing the skin friction whilst the vessel is in motion, seriously reduce its speed, and it is by no means an uncommon thing for a tramp steamer, with a normal speed of 9 knots, to be reduced to 5 or 6 knots by such fouling.

The nature of these growths needs to be studied in properly equipped marine biological laboratories, as but little is at present known of the life-history of many of the organisms which are found on a ship's bottom. The main factors, however, are that it is only during the germ or spore period of their existence that they can attach themselves to the bottom of the vessel, and that although the full-grown results are found when the vessel is docked, these growths have taken place *in situ*.

The open ocean and the northern seas are comparatively free from these organisms, but directly inland seas or tropical waters are reached they increase to an enormous extent in variety and numbers, and some harbours, such as the port of Sourabaya, are noted for the fouling influence of their waters. Moreover, it is found that the period of the year exercises a very important influence upon the fouling nature of the water, the spring and early summer being the chief time for these growths to find a lodgment on the bottom of a vessel.

The more common growths are serpulæ, generally called coralline, barnacles, mussels, membranæ, and oysters, usually classified together under the name of 'shell,' whilst at or near the water line are found luxuriant growths of sea grass (*Enteromorpha compressa* and *Zostera marina*), and towards the bottom ribbon and other weeds, like the tufted weed or bugula, flourish.

Fouling commences with the deposition of a slight slime on the side of the vessel, which is apparently of an albuminous nature, and contains the germs and spores of various marine growths, and is so slight as to escape notice.

The first visible sign of fouling on a ship is the appearance of green grass at the water line, and this, in bad waters, will begin to show after a few weeks, whilst the growth will spread downwards from the surface for 5 or 6 feet, but rarely extends below 10 feet, as the growth needs plenty of light and warmth.

It is the most widely distributed form of fouling, and appears in nearly all waters, and, once formed, the grass protects the germs of other growths, and so helps on the general fouling.

In northern waters fouling seldom goes beyond the 'grass,' but in warm climates, especially if long in port, 'shell' soon begins to appear, unless a really good anti-fouling composition is employed for coating the vessel's bottom.

Ships trading to or stationed near the mouths of rivers often show curious results in the kind and extent of the fouling, the marine growths being often killed by the fresh water, but such vessels foul again very rapidly when once more going to sea, owing to slight deposits of mud and calcium carbonate from the river water.

With wooden ships the necessity of protection against the wood-boring teredo worm as well as fouling led to the adoption of copper sheathing, and when the metal used was of a fairly pure character, it was found to be thoroughly satisfactory, and not only to give complete protection to the vessel, but also to enable it to remain at sea for a very considerable period. The cost, however, was high, and attempts were made to prevent the excessive waste of the copper by using zinc protectors, as advocated by Sir Humphry Davy, but it was soon found that with the prolongation of the life of the copper plates, fouling again became serious, whilst when later rolled sheets of alloys containing zinc, such as Muntz metal, were tried, the same trouble again appeared, and it has been clearly proved that the power a copper plate exercises in preventing fouling is inversely proportional to its power of resisting the action of the sea water.

The action of the copper in anti-fouling is that, in the first place, the salts in solution in the sea water act upon the copper with the formation of chlorides and oxychlorides, the former poisonous to all forms of marine life in the germ state, whilst the latter formed a coherent pellicle to which the growths attached themselves and which was torn off during the passage of the vessel through the water by the skin friction, thus enabling it to shed any form of growth that might have attached itself to the plate.

It was found, however, that if the copper were not of the purest, coralline growths very soon attached themselves so firmly through the surface of the skin of copper compounds that it was difficult to remove, and gave points of adherence for fresh vegetable growths.

With the introduction of steel and iron ships, as was natural, attempts were made to utilise the same form of protection from fouling which had proved so satisfactory with wooden ships, and from time to time during the past 80 years efforts have been directed to sheathing iron ships with copper in the same way. It was soon found, however, that this sheathing set up such severe galvanic action with the hull of the vessel as to be impracticable, and although these attempts were abandoned at a very early period in the mercantile marine, the naval services of several countries have tried its use for service vessels, the generally adopted method being to sheathe the iron hull with wood and to attach to this the copper in such a way as to be insulated from the electro-positive iron.

These experiments met with more or less success, but with increase in dock accommodation, the tendency has been more and more towards the use of anti-fouling paints or compositions, which could be painted on over the protective coating of the vessel, and some 80 compositions have been placed on the market with varying success for this purpose.

When anti-fouling paints were first manufactured, the only fact at the service of the maker was the experience which had been gleaned from copper sheathing, and on the assumption that the action had been due to the poisonous character of the chloride and oxychloride of copper produced on the plates by the salts in the sea water, compositions were made containing large quantities of corrosive metallic poisons, which, held in a varnish of a more or less lasting character, gave the protection from fouling for a few months.

As has already been pointed out, the action of the copper sheathing was due to two causes: first, the poisonous action of the copper salts on the germ life; and, secondly, the stripping of the pellicle by skin friction when any quantity of growth had formed on its surface, an action termed 'exfoliation.' How important this latter action was may be judged from the fact that when the vessel remained at anchor in a harbour, the sheathing would last from 10 to 12 years, whilst when on active service the same sheathing would last for only 4 or 5.

Finding that poisons alone gave very unsatisfactory results, the manufacturers of anti-fouling compositions began to make perishable varnishes and grease paints, which should, by the deterioration and wasting of their surface, imitate as nearly as possible the exfoliation of the copper sheathing, and such anti-foulers gave under certain circumstances much more successful results. The idea was that the ship, having been coated with a protective paint or composition to preserve the iron, a second or more coatings was put on over the protective, consisting of varnish paints which should slowly yield soluble poisons to the sea water, and in doing so would lead to the disintegration of the varnish surface, which, being washed off, exposed fresh quantities of the poisons to the water.

Such compositions proved very satisfactory in the mercantile marine, and all the time that a vessel was actively engaged in going from port to port gave excellent results, but directly these same compositions, which had gained a reputation in the merchant service, were tried on Service vessels, they were found to be as unsatisfactory as those which before had been in use. The reason for this failure is evident. Take the case of a liner trading between New York and England: she is run at a high speed between these two ports for the main portion of her life, remaining in the basin for as short a period as possible in order to utilise to the full her money-earning capacity; for such works it is easy to arrange an anti-fouling composition, which, with the aid of the skin friction of the vessel, would cause just sufficient wasting of the coating to give the best results. When, however, this is applied to a Service vessel, she probably goes out from dock into the basin and remains there stationary for perhaps months, and then goes to sea, where she is kept manœuvering at various rates of speed for a considerable period. During the period she is in the basin, the composition undergoes practically no wasting, and a thin film of carbonate of lime and mud deposits on the surface, which forms an excellent foothold for any germs and spores that may be in the water, and which, on going to sea, have often advanced too far for the growth to be readily got rid of.

The bad results so obtained led to a composition being put on which wasted with sufficient rapidity to prevent any such deposition in harbour, with the result that when the vessel went to sea, the deterioration being accelerated

to an enormous extent by skin friction, the composition was practically all exhausted in a very short time.

In the Service this trouble will never be got rid of until the painting of the bottoms of the vessels is placed in the hands of an expert, with a knowledge of the work which a vessel has to perform, and who can adjust the composition to the duty which has to be done. In the merchant service, where this is well known and can be provided for, very little trouble now exists.

The most efficient anti-fouling compositions all contain copper or mercury as the poison. In some cases soluble salts of these metals are employed with a fairly strong and lasting varnish; in others oxides or insoluble salts are used with varnishes which perish more rapidly on their surfaces and allow the action of the sea water to convert the compounds into soluble salts.

It is evident that with compositions containing such metallic compounds every attention must be paid to the protection of the hull, as otherwise the formation of soluble salts of copper and mercury might result in the deposition on the iron of these metals by reduction, in which case rapid galvanic action would be set up, and would lead to serious pitting of the plates of the vessel.

The compositions of the present day may be divided into two classes:

1. Grease paints containing a metallic poison;
2. Quick-drying varnish paints, also charged with the same poisonous constituents.

The former class has met with a considerable degree of success, but they have also several very serious drawbacks. As regards the prevention of fouling, they give results not very far removed from the best varnish paints, and in certain waters, such as the Mediterranean, have proved themselves to be excellent anti-foulers, but they undoubtedly increase the skin friction of the vessel, and so tend to diminish speed; whilst a second trouble is that, although a varnish paint may often be scrubbed and touched up where fouling has been but slight, with a grease paint the whole has to be removed before recoating, and they are much more costly than the varnish paints, with the result that in the merchant service they are used only to a very limited extent. Another drawback to their use is that it is impossible to properly scrape and recoat the vessel during the short period of docking which would suffice for a varnish paint.

In the manufacture of varnish paints it is necessary to mix with the solution of gum or resin in a volatile solvent a sufficient proportion of linseed oil to give elasticity to the vehicle, and these paints have been in use in England since about 1870, the greatest advance in them being due to the introduction of the hot process in their manufacture, which enables a more intimate mixture to be made with greater adhesive power and a smoother surface.

The rate at which disintegration of these paints takes place is governed largely by the kind of gum used in the varnish, and by the amount of mineral matter introduced as colouring and poisonous material, the solubility of these having a considerable influence on the rate of disintegration.

With a tough and tenacious vehicle, which by itself would undergo but little disintegration under the action of sea water, it is quite possible to use soluble mercury or copper salts, which are liberated only very slowly during the gradual destruction of the varnish. On the other hand, if a rosin varnish be employed, insoluble bodies, like the oxides of copper and mercury, the sub-chloride of mercury, or Scheele's green (copper arsenite) may be used, the oxides and other salts, when exposed to the sea water, being very slowly converted into soluble chlorides.

Many compositions contain arsenic and arsenic compounds, such as sodium arsenite, as these had been found effective as weed killers under ordinary conditions, and it was expected that in a composition they would prevent the growth of grass at the water line, which, as it caught the eye, gave the impression of the ship being very foul. Experience showed, however, that the arsenic had but little effect, and mercury and copper still remain pre-eminently the metallic poisons of the greatest value in anti-foulers.

One of the most difficult portions of the ship to deal with is what is known as the 'boot top,' that is, the portion between the heavy and light load line, as when a ship is discharging cargo the anti-fouling composition over this portion is exposed to the sun and rapidly perishes and peels off, whilst when the ship is again loaded, it is once more immersed, and the alternate action of sunshine and air and sea water perishes the paint at the very spot where it is most likely to be abraded by contact with lighters and barges, the result being that it is often necessary to touch up this portion of the vessel with paint during the voyage, and as good anti-fouling paints are rarely carried for this purpose, this portion of the ship is often painted with ordinary paint, and hence is liable to more damage than other parts of the vessel.

In some anti-fouling varnish paints the poisonous metals themselves have been carried in a very fine state of division, some paints containing very finely divided copper, precipitated from the solution of a copper salt by iron or zinc; whilst others contain metallic mercury in a comminuted condition, obtained by adding stannous chloride to the solution of a mercurous salt; these paints, however, show but little advantage over those containing salts of the metals.

V. B. L.

CORROSIVE SUBLIMATE (*Mercuric chloride*) *v.* MERCURY.

CORUBIN *v.* ABRASIVES.

CORUNDUM. (*Corindon*, Fr.; *Korund*, Ger.) Native alumina; so called from its Sanskrit name *korund*, whence it is assumed that the mineral was originally brought to Europe from India. From its hardness, which is second only to that of the diamond, it is sometimes known as *adamantine spar* (*Diamantspat*, Ger.). Emery is an impure variety, never crystallised (*v.* EMERY). Corundum crystallises in the rhombohedral system, usually in double six-sided pyramids and rhombohedra, with the basal plane. The crystals sometimes show a lamellar parting parallel to the faces of the rhombohedron or the base. The lustre is vitreous, and

therefore different from that of diamond; some varieties exhibit a pearly lustre on the basal plane. It is optically uniaxial; double refraction negative, $\omega = 1{\cdot}769$, $\epsilon = 1{\cdot}759$. The coloured varieties are markedly pleochroic. H. 9; sp.gr. 3·9–4·1. Infusible before the blowpipe; but with borax fuses, with difficulty, to a clear glass. Unattacked by acids. The fine powder, strongly heated with cobalt solution, gives the characteristic blue colour of alumina.

The dull-coloured and opaque varieties, to which the term 'common corundum' is sometimes applied, occur chiefly in India, China, Siberia, and the United States. The mineral has been obtained for ages from the old crystalline and metamorphic rocks of Southern India, notably from the Salem district, Madras. Large deposits of grey, red, or purple tints occur near Singrauli, in South Rewah, where it is systematically worked. The hardness of the mineral renders it difficult of extraction, and fire is often lighted against the face of the rock to aid in loosening fragments. According to Newbold, the Indian corundum occurs in gneiss, mica-schist, or hornblende-schist. (On Indian corundum, *v.* T. H. Holland, Man. Geol. Ind. 2nd ed. 1898.)

In America large deposits of corundum occur in the older rocks of the Atlantic States, especially in North Carolina and Georgia. In 1871 it was discovered by C. W. Jenks at Corundum Hill, Macon Co., North Carolina, where the common varieties passed into brightly coloured transparent forms, sufficiently fine in some cases to be cut as gem-stones, and interesting as affording the first instance of the occurrence of ruby and sapphire in their original matrix (Quart. J. Geol. Soc. 30, 1874, 303; J. W. Judd and W. E. Hidden, Min. Mag. 1899, xii. 139).

This deposit, as well as that at Laurel Creek, Georgia, has been extensively mined. The corundum at both localities occurs in association with peridotite and hornblende-gneiss. Blocks weighing as much as 5000 lbs. each have been extracted. The corundum is prepared for the market by a succession of crushings and washings, the dressed mineral being finally sifted so as to separate it into various grades of fineness, distinguished in trade by numbers; the finest being known as 'flour.' The crushing is performed by means of stamps and rollers, but these require frequent repair in consequence of rapid wear due to the extreme hardness of the mineral. It is more difficult to crush corundum than emery, in consequence of its superior hardness.

Corundum is largely used as an abrading agent. Taking the abrasive power of sapphire as 100, that of the American corundum varies from 90 to 97, while that of Naxos emery is only between 40 and 57. The abrasive power, or 'effective hardness,' is estimated by rubbing a weighed sample of the mineral on a piece of plate-glass; the glass is weighed before commencing the operation, and is re-weighed from time to time during the grinding, when its loss affords an estimate of the abrading power of the substance. Of late years corundum has been largely used in the form of 'corundum wheels,' which are prepared by incorporating the coarsely crushed mineral with a medium that admits of being readily moulded. (On American corundum, *v.* J. H. Pratt, Bull. U. S. Geol. Surv. No. 269, 1906; J. H. Pratt and J. V. Lewis, North Carolina Geol. Surv., i. 1905.)

The transparent variety of corundum, when cut and polished, is highly valued as a gem-stone. When blue, it is termed *sapphire*, while the clear colourless stones often pass under the name of *white sapphire*. The red varieties are known as *ruby*, or as *oriental ruby*, the qualifying word being used to distinguish it from inferior stones, such as spinel, which are also termed 'ruby' ('spinel-ruby' and 'balas-ruby') *Barklyite* is a turbid magenta-tinted corundum from Victoria. The other coloured corundums are generally known as 'oriental' stones; thus the yellow varieties, though sometimes called *yellow sapphire*, are usually termed '*oriental topaz*'; the purple stones are distinguished as '*oriental amethyst*'; and the green corundum, which is the rarest of all, is prized as '*oriental emerald*.' The following analyses of some typical forms of corundum were made by J. Lawrence Smith (Amer. J. Sci. 1851, [2] 11, 54):

	Al_2O_3	Fe_3O_4	SiO_2	CaO	H_2O
Sapphire (India)	97·51	1·89	0·80	—	—
Ruby (India) .	97·32	1·09	1·21	—	—
Corundum (India)	93·12	0·91	0·96	1·02	2·86
Corundum (Asia Minor) . .	92·39	1·67	2·05	1·12	1·60

It is believed that the ruby owes its colour to the presence of oxide of chromium. When strongly heated, it becomes green, but regains its normal colour on cooling. The nature of the colouring matter of sapphire is not well understood; and though cobalt has been suggested, its presence has not been proved, and it seems likely that some compound of chromium is here also the tinctorial agent. Certain sapphires become decolorised by heat. It is notable that in many sapphires the pigment is locally distributed, so that the stone is parti-coloured.

Haidinger's dichroscope, which is frequently used to distinguish one gem-stone from another, may sometimes be usefully applied to the coloured corundums. In many sapphires the two images differ greatly in tint, one being dark blue while the other is pale bluish-green, or even yellowish; in other sapphires, however, the difference of tint is very slight. In dealing with highly pleochroic stones, the phenomenon may be observed with the unaided eye. Thus certain sapphires appear blue when viewed in the direction of the optic axis or along the principal axis of the prism, and green at right angles to this direction or perpendicularly to the prismatic faces. In ruby the dichroism is not so marked as in sapphire. Viewed in the dichroscope, one image may be deeper than the other; the red of the one inclining to violet, that of the other to yellow.

The ruby may be distinguished from all other red stones by its superior hardness. From spinel and rubellite it may be separated by its high sp.gr. If the dichroism can be detected, this character will distinguish it from either garnet or spinel, since these minerals crystallise in the cubic system, and are consequently not pleochroic.

Coloured corundums frequently contain minute fluid cavities and microscopic crystals, which have been studied by H. C. Sorby and

P. J. Butler (Proc. Roy. Soc. 17, 1869, 291). According to these observers, the fluid cavities are more numerous in sapphire than in ruby; while the enclosed crystals are more abundant in ruby than in sapphire. The inclusions often give a milky and defective appearance to the stone, and when definitely orientated produce curious optical phenomena. It seems due partly to these lines of inclusions, and partly to a system of striations intersecting at 60°, that certain corundums, when cut with a convex surface, display by reflected light a luminous six-rayed star. This phenomenon is not uncommon in blue-grey opalescent sapphires, which are consequently known as *asterias* or *star-sapphires* (*Saphir astérié*; *Sternsapphir*). It is notable that the hardness of the sapphire slightly exceeds that of the ruby.

Sapphires are found as rolled crystals and pebbles in detrital deposits in Ceylon; and they occur with rubies in Upper Burma. Some years ago fine sapphires were discovered in the Zanskar range of the Himalaya Mountains; and large deposits of dark-coloured stones have been found in the province of Battambang in Siam. Near Helena, in Montana, U.S., rolled crystals of sapphire are found in placer mining. In Europe small sapphires occur in certain basaltic rocks, as in the Siebengebirge on the Rhine, and at Expailly, near Puy-en-Velay in France; but the European stones are worthless.

Sapphire is not uncommon in the gold-bearing drifts of New South Wales and Victoria, but the ruby is rare. The late A. M. Thomson, of Sydney, made the following analyses, cited by A. Liversidge, in the Min. of N. S. W. 1888, 196:—

	Al_2O_3	Fe_2O_3	CaO	MgO
Sapphire (Mudgee) .	98·57	2·25	0·45	—
Ruby (Two-Mile Flat)	97·90	1·39	0·63	0·52

Most, if not all, of the so-called 'Australian rubies' and 'Adelaide rubies' are merely garnets. In like manner, the garnets from the diamond-mines at Kimberley pass in trade under the name of 'Cape rubies.'

The true ruby is of much more limited distribution than the sapphire. It occurs but sparingly in the gem-bearing detritus of Ceylon, where sapphires are common. The chief ruby locality is at Mogok, in Upper Burma, where the rubies occur in detrital deposits and in a bed known locally as *byon*. The mother rock of the Burmese ruby is a white crystalline limestone occurring as thick bands, interfoliated with gneisses (C. B. Brown and J. W. Judd, Phil. Trans. 1896, 187, A, 151; T. H. Holland, *l.c.*).

The artificial production of ruby has been effected at various times by Gaudin, Elsner, Ebelmen, De Senarmont, Sainte-Claire Deville, and Caron and Debray; but it was not until the experiments of Fremy and Feil in 1877 that the substance was obtained well crystallised in any quantity. By fusing a mixture of alumina and red lead in a fireclay crucible, these experimentalists obtained a fused aluminate of lead, which was decomposed by the silica of the crucible with formation of silicate of lead, while free alumina crystallised out, on cooling, as white corundum. By the admixture of from 2 to 3 p.c. of potassium dichromate with the original materials, the resulting alumina separated in the form of ruby, while the association of a small proportion of oxide of cobalt with the potassium dichromate determined the production of sapphire (Compt. rend. 1877, 85, 1029). E. Fremy and A. Verneuil also obtained fine artificial rubies by the reaction of barium fluoride at a red heat on amorphous alumina containing traces of potassium dichromate. The substance thus obtained possesses all the physical characteristics of natural rubies, and Des Cloizeaux has shown that they agree in crystalline form (Compt. rend. 1888, 106, 565, 567).

The jewellery trade was much disturbed about 1886 by the appearance of large numbers of rubies of fine colour sold by a house in Geneva. Having excited suspicion, the stones were placed in the hands of C. Friedel for examination. He found them to agree with the natural ruby in all respects, except that they contained little spherical blebs, readily seen with a hand-lens, whence he concluded that they had been formed by the fusion of a number of small rubies. Stones of small size are of comparatively little value, while a large ruby, of fine colour, always commands a very high price. Terreil and Verneuil have fused amorphous alumina in the oxyhydrogen blowpipe, and E. Jannettaz has examined the behaviour of this product when subjected to electric discharge in Crookes' exhausted tubes, and found it to agree with that of the Geneva rubies and the natural corundum by glowing with a vivid red light (Bull. Soc. Fr. Min. 9, 1886, 321).

In 1904, A. Verneuil devised a still more successful process, by which fine gem-stones of almost any size can be produced with ease. The material he uses is pure alumina (precipitated by ammonia from a solution of ammonium-alum), which, in a powdered form, is fed through the oxygen tube of an inverted oxygen-coal-gas blowpipe. The alumina falls as a molten drop on a pedestal beneath, and there crystallises as corundum. As the operation is continued, the corundum grows upwards as a pear-shaped drop or 'boule.' Although these drops have a smooth rounded exterior, with no external crystal faces, they each consist of an individual crystal with an internal crystalline structure, and identical in all their characters with naturally occurring corundum. From natural corundum they can only be distinguished by the presence of microscopic air bubbles, and very fine internal streaks, which are curved (and not straight, as in the natural stone). When the alumina is quite pure, and no colouring materials have been added, the artificial corundum so prepared is colourless: a fine ruby-red colour results by the addition of some chromium-alum to the ammonium-alum. Attempts to produce a sapphire-blue colour by the addition of cobalt at first were not successful, but this has been obtained by adding magnetic oxide of iron (1·5 p.c.) and titanium dioxide (0·5 p.c.) (Compt. rend. 1910, 150, 185). Excellent gem-stones are now produced in large quantities by this process. L. J. S.

CORYBULINE, CORYCAVINE *v.* VEGETO-ALKALOIDS.

CORYDALINE *v.* VEGETO-ALKALOIDS.

CORYFIN. Trade name for ethyl glycoilic menthyl ester $C_{10}H_{19}O{\cdot}CO{\cdot}CH_2{\cdot}O{\cdot}C_2H_5$ used in the treatment of nasal catarrh.

COSMOS REDS *v.* AZO- COLOURING MATTERS

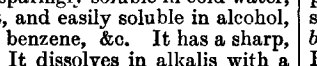
COTO BARK. True coto bark is obtained from Bolivia, the Amazons (Brazil), and Venezuela. It has been considered identical with Winter's bark [from *Drimys Winteri* (Forst.)], but its source is really unknown (Jobst and Hesse, Annalen, 282, 191). It comes into the market in long strips about 8 cm. broad and 12 mm. thick, and is tough and hard. The colour is cinnamon brown, and a cross section shows numerous yellow spots. It has an aromatic odour, and contains *cotoïn*, *dicotoïn*, *hydrocotoïn* and *methyl-hydrocotoïn*, resins, tannin, &c. The supply of the true coto bark is limited, so inferior barks, chiefly *para-coto bark*, are sold. These contain little or no cotoïn, but instead *protocotoïn* and *methyl-protocotoïn*.

Cotoïn is the monomethyl ether of benzoylphloroglucinol $C_6H_5{\cdot}CO{\cdot}C_6H_2(OH)_2{\cdot}OCH_3$ (Ciamician and Silber, Ber. 1894, 27, 409; Pollak, Monatsh. 1901, 22, 996). It is the active principle of coto bark, and is obtained by extracting the bark with ether, evaporating the solution, adding light petroleum to precipitate the resin, decanting off the solution and allowing to crystallise (Jobst and Hesse, Annalen, 199, 17). Cotoïn forms pale-yellow prisms or tables, m.p. 130°, sparingly soluble in cold water, more easily in hot, and easily soluble in alcohol, chloroform, ether, benzene, &c. It has a sharp, astringent taste. It dissolves in alkalis with a yellow colour, and in nitric acid with a deep-red colour. The alcoholic solution gives a red-brown colouration with ferric chloride, and on boiling a rich brown precipitate is obtained.

Cotoïn is used therapeutically in the treatment of diarrhœa, cholera, colic, &c., and for rheumatism, neuralgia, and gout. The dose is: for children, 0·05–0·15 gram; for adults, 0·20–0·60 gram. It is also administered in ethereal solution by subcutaneous injection.

An extract of the bark may be used medicinally, but has unpleasant after-effects.

Dicotoïn $C_{25}H_{20}O_6$ is probably a compound of cotoïn and phenyl-coumalin



(Ciamician and Silber, Ber. 1895, 28, 1549). It is obtained by boiling cotoïn with water, and forms lustrous, colourless plates, m.p. 74°–77°, easily soluble in alcohol, ether, &c. (Jobst and Hesse, *ibid.* 1878, 11, 1031).

Hydrocotoïn, methyl cotoïn

$$C_6H_5{\cdot}CO{\cdot}C_6H_2(OH)(OCH_3)_2$$

forms brilliant, pale-yellow prisms, m.p. 98°, soluble in alcohol and in boiling water.

Methyl-hydrocotoïn $C_6H_5{\cdot}CO{\cdot}C_6H_2(OCH_3)_3$, obtained from coto bark or by the methylation of hydrocotoïn, forms small colourless crystals, m.p. 113° (Ciamician and Silber, Ber. 1893, 26, 2340; 1894, 27, 419).

Protocotoïn

$$(CH_3O)_2(OH){\cdot}C_6H_2{\cdot}CO{\cdot}C_6H_3(O_2CH_2)$$

forms bright-yellow monoclinic prisms, m.p. 141°–142°. It is soluble in organic solvents but insoluble in water.

Methyl-protocotoïn

$$(CH_3O)_3{\cdot}C_6H_2{\cdot}CO{\cdot}C_6H_3(O_2CH_2)$$

crystallises from alcohol in colourless prisms, m.p. 134°–135° (Ciamician and Silber, Ber. 1891, 24, 2977).

Hesse has examined a coto bark from Bolivia, which contained no cotoïn, but a neutral substance, *cotellin* $C_{18}H_{16}O_4(OCH_3)_2$, which forms glistening leaflets or pyramids, is tasteless, and melts at 169° (J. pr. Chem. 1905, 72, 243).

COTTON consists of the long hairs which cover the seeds of various species of *Gossypium*, a genus of the nat. ord. *Malvaceæ*. The botanical classification of cotton is in a confused state, and this is doubtless mainly due to the cultivation of the plant for extensive periods, the large interchange of seed which has taken place between the different countries of production and the consequent gradual modification of the distinctive characters of the original species.

American cottons.—The ordinary Upland cotton is fairly generally considered to be derived from *Gossypium hirsutum* (Linn.). Some authorities, however, are of opinion that it is derived from *G. herbaceum* (Linn.), whilst others regard these two species as identical. Sea Island cotton has usually been regarded as *G. barbadense*, but is considered by Watt (Wild and Cultivated Cotton Plants of the World) to be a hybrid form.

Egyptian cottons.—The Egyptian cottons probably cannot be referred to any particular species, but are mostly hybrid forms of *G. barbadense* with other species. Most commonly, Egyptian cottons are regarded as *G. barbadense*, but Watt places them under *G. peruvianum* (Cav.), which some authorities consider as identical with the former.

Indian cottons.—With reference to these varieties, G. A. Gammie, of the College of Science, Poona, writes, in his monograph on The Indian Cottons: 'It is clearly evident that we have at the most only one true species of cotton in India, *Gossypium obtusifolium*, with its two sub-species, *G. arboreum* and *G. herbaceum*. All other forms should be treated as derivatives of these.' Other botanists, however, regard the Indian cottons as derived from various distinct species, including *G. herbaceum*, *G. neglectum*, *G. Wightianum*, and *G. arboreum*.

Brazilian and *Peruvian cottons.*—Brazilian cotton is generally considered to be the product of *G. brasiliense* (Macf.), and rough Peruvian cotton that of *G. peruvianum* (Cav.).

The cotton plant grows as a shrub or small tree. It is of perennial habit, but, in cultivation, is usually treated as an annual. In certain districts of Brazil and Peru, however, arborescent forms are grown, which are allowed to remain in the ground for several years. When the flower-bud first opens, the petals are generally white or pale yellow, but they gradually become darker and redder until the third or fourth day, and then fall to the ground. The young fruit remains attached to the flower-stalk and enveloped in the calyx; it gradually increases in size, and is known as the 'boll.' When the boll is ripe, it dehisces by from three to five valves, exposing the cotton, which, now that the pressure on it is released, rapidly expands and forms a large fluffy mass. As soon as the boll has opened completely, and is quite dry, the cotton is ready to be gathered. The seeds, with the cotton fibre adhering to them, form the product known as 'seed cotton'; this is collected from the ripe bolls, and the cotton (or 'lint'), after being torn from the seeds by

the process of 'ginning,' constitutes the raw cotton of commerce. Seed cotton usually consists of about one-third of its weight of cotton fibre and two-thirds of seeds.

The cotton fibre is composed of a single hollow cell, and, while unripe, has the form of a long narrow tube. As the fibre matures, it becomes more or less flattened, and presents the appearance of a narrow, somewhat opaque ribbon or band, with slightly thickened, rounded edges. The ripe fibre possesses a peculiar characteristic twist. This twist appears to be an acquired character; it is not present in wild cotton, and is increased by care in cultivation. The number of twists in a given length is very variable, and, as a rule, is, roughly speaking, inversely proportional to the diameter of the fibre, the twist being most numerous in the finest variety (Sea Island). Unripe cotton consists of thin, transparent fibres with little or no twist. Such fibres are known technically as 'dead cotton,' and, being very weak and brittle, they break up in the process of manufacture, thus increasing the amount of waste, and also tending to weaken the yarn or fabric into the composition of which they enter; they also possess the defect of not being able to take dyes satisfactorily.

According to the length of the individual fibres, cottons are classed in commerce as long-, medium-, or short-stapled. The long-stapled cottons are 1¼ inches or more in length, the medium-stapled are about 1 inch long, and the short-stapled are less than 1 inch. The principal long-stapled varieties are Sea Island cotton, Egyptian varieties, and the improved American Upland forms, which have been evolved from the ordinary Upland kinds by continuous selection and careful cultivation. The Brazilian and Peruvian cottons vary from about 1 to 1½ inches, and are, therefore, either medium- or long-stapled. The chief medium-stapled cottons are the ordinary American Upland kinds, and the short-stapled class is represented by the Indian varieties.

Sea Island cotton is grown in South Carolina, Georgia, Florida, and the West Indies. The fibre is very long, fine, silky, and of a lustrous creamy tint, and this cotton is therefore the most valuable variety. It is used in commerce for spinning the finest and best yarns. Considerable care is required in the cultivation of this cotton, and the yield per acre is usually lower than that of other kinds.

American Upland cottons are produced in enormous quantities in the United States, and are the principal kinds used in the Lancashire spinning industry. They are of longer staple and better quality than the Indian varieties, and are employed for the manufacture of yarns of medium quality.

Egyptian cottons exist in several varieties, most of which yield a fibre of a brownish tint. These cottons are long, strong, and fine, and more lustrous than American Upland, but inferior to Sea Island cotton. Egyptian cotton is preferable to American Upland for the manufacture of goods requiring a soft, smooth finish and high lustre.

The Indian cottons are mostly short and coarse, and are consequently less valuable than American Upland kinds. The chief markets for these varieties are Japan and Germany, comparatively little being imported into the United Kingdom.

Brazilian cotton is harsh and wiry, of medium strength and of good length. One of the varieties grown in North Brazil is a tree cotton, which lives for 8 years or more. The ordinary annual cottons are more largely cultivated and are more productive than the arborescent form, but the fibre of the latter has the longer staple.

Peruvian cotton is chiefly of two kinds, known respectively as 'rough' and 'smooth.' The former is the product of a tree cotton which is allowed to remain in the ground for from 4 to 6 years; the fibre is well known for its peculiarly harsh and crinkly character, which renders it especially useful to spinners for mixing with wool. 'Smooth' Peruvian is very similar to American Upland cotton, and is used for the same purposes.

The following table gives the approximate length and average diameter of the fibres of the principal commercial varieties. The diameters of the fibres of any one variety show great variation among themselves, but the figures given under this head are the average of a large number of determinations by various observers, and can, at least, be regarded as relatively accurate:—

Variety	Usual length	Average diameter
	inches	inch
Sea Island . .	1·6–2·2	0·00064
American Upland .	0·8–1·1	0·00077
Egyptian . . .	1·3–1·6	0·00068
Indian . . .	0·6–1·0	0·00084
Brazilian . . .	1·1–1·4	0·00080
Peruvian (rough) .	1·2–1·5	0·00078
„ (smooth) .	0·9–1·1	0·00077

Cotton consists of about 90 p.c. of cellulose (*q.v.*), together with 7–8 p.c. of water, 0·4 p.c. of wax and oil, 0·6 p.c. of nitrogenous substances, and about 1 p.c. of mineral matter (ash).

The wax is present as a thin layer on the surface of the fibre, and renders it incapable of absorbing water readily. This substance, to which Schunck (Manchester, Mem. Lit. Phil. Soc. [iii.] 4, 95) has given the name 'cotton wax' resembles other vegetable waxes, such as cerosin prepared from the leaves of the sugar-cane, and the waxes from the leaves of the carnauba palm [*Copernicia cerifera* (Mart.)], and the raphia palm [*Raphia pedunculata* (Beauv.). It is insoluble in water, but soluble in alcohol or ether; it melts at 86°, and solidifies again at 80°–82°. Pure cotton wax is insoluble in solutions of caustic alkali; it contains C 80·4, H 14·5, O 5·1. Associated with this wax is a fatty acid, which was regarded by Schunck as margaric acid, but is more probably a mixture of stearic and palmitic acids; it melts at 55·5°, and resolidifies at 50·5°.

The oil in the cotton fibre appears to be identical with that contained in the seed. In the preparation of the so-called absorbent cotton wool, the wax and oil are removed by boiling the fibre with dilute caustic alkali under pressure; the material is subsequently washed, treated

with bleaching powder and hydrochloric acid, again washed, and dried.

The nitrogenous constituents of cotton consist of the remains of the cell protoplasm and allied substances.

The mineral substances contained in the fibre are chiefly phosphates, chlorides, and sulphates of potassium, sodium, magnesium, and calcium, together with small quantities of iron and traces of aluminium. If the amount of ash is much more than 1 p.c., the excess is probably due to the presence of sand and other mechanical impurities.

When cotton is immersed in a strong solution of caustic soda, it undergoes certain remarkable changes, the chief of which is the production of a silky lustre. This phenomenon was discovered by John Mercer in 1844, and has led to results of great commercial importance. The process is now carried out on an extensive scale under the name of 'mercerisation' (*q.v.*), and is sometimes applied to the yarn and sometimes to the woven fabric. The material is either kept in a state of tension during the operation, or is allowed to shrink in the alkaline liquid, and afterwards stretched to its original length before being washed. The process not only produces an exceedingly high lustre on the cotton, but also increases its power of absorbing dyes. The structure of the cotton fibre undergoes alteration; the flattened, twisted tube, characteristic of ordinary cotton, swells out, and is thus converted into a hollow, cylindrical form. This change is accompanied by a decrease in length and also by an increase in tensile strength, mercerised cotton being in some cases as much as 50 p.c. stronger than ordinary cotton. Egyptian cotton generally mercerises better than ordinary American cotton.

When cotton is treated with a mixture of nitric and sulphuric acids, it is converted into nitro-cellulose or gun-cotton (*v.* EXPLOSIVES). On dissolving gun-cotton in ether, or a mixture of ether and alcohol, the product known as collodion is obtained (*v.* PHOTOGRAPHY). Nitro-cellulose also enters into the composition of celluloid (*q.v.*).

Among the more important works on this subject may be mentioned The Cotton Plant, Bull. No. 33, Office of Expt. Stat. U.S. Dept. of Agric.; Bowman's Structure of the Cotton Fibre; and Oppel's Die Baumwolle. E. G.

COTTON BROWNS, SCARLETS, YELLOWS, *v.* AZO- COLOURING MATTERS; PRIMULINE.

COTTON FLOWERS. Among the various portions of the cotton plant which have been industrially employed must be included the flowers which constitute one of the numerous Indian dyestuffs. According to Watt (Dictionary of the Economic Products of India), they are thus utilised in the Manipur district.

Gossypetin $C_{15}H_{10}O_8$. The flowers are extracted with boiling alcohol, the extract evaporated, treated with water, and the mixture extracted with ether to remove chlorophyll and wax. The aqueous solution, containing the glucoside of gossypetin, is digested at the boiling temperature with sulphuric acid, and, on cooling, a precipitate of the crude colouring matter separates. It is dissolved in alcohol, the solution poured into ether, and, after removal of precipitated impurities, the liquid is washed with water and evaporated. The yellow residue is best purified by acetylation, and the acetyl derivative, after repeated crystallisation from alcohol, is hydrolysed in the usual manner (Perkin, Chem. Soc. Trans. 1899, 75, 826). Gossypetin forms yellow needles, closely resembling quercetin in appearance, and is readily soluble in alcohol, but only very sparingly in water. Concentrated alkaline solutions dissolve it, forming orange-red solutions, which, on agitation and dilution with water, become green, and finally assume a dull-brown tint. Alcoholic lead acetate gives a deep-red precipitate in the cold, passing into dull-brown at the boiling-point, and alcoholic ferric chloride a dull olive-green liquid.

Gossypetin, like quercetin, forms compounds with mineral acids which crystallise in orange-red needles, and with alcoholic potassium acetate the monopotassium derivative $C_{15}H_9O_8K$ is produced. The *hexacetyl* derivative

$$C_{15}H_4O_8(C_2H_3O)_6$$

forms colourless needles, melting at 226°–228° (*ibid.* 1909, 95, 2188). By fusion with alkali, *protocatechuic acid* and a phenol, the identity of which has not been established, are produced.

On mordanted wool gossypetin gives the following shades:—

Aluminium	*Tin*	*Chromium*	*Iron*
Pale orange brown	Orange red	Dull brown	Deep dull olive

With aluminium mordant, the results vary greatly, according as chalk is present or absent in the dye bath, a result evidently due to the ready oxidation of gossypetin in the presence of alkalis or alkaline earths. Thus if the mordanted wool, which is of an acid nature, is employed alone, the above shade is produced; but if chalk is added, a deep olive-yellow is obtained. Calico mordanted with aluminium, being of a basic nature, yields this olive-yellow shade without the employment of chalk.

Gossypitrin $C_{21}H_{20}O_{13}$, the glucoside of gossypetin, is isolated with difficulty, and has only been prepared in very small quantity. This arises from the fact that the flowers (that is, the Egyptian variety) also contain the two glucosides *quercimmeritrin* and *isoquercitrin* (*see* glucosides of quercetin), and the separation of the three substances involves many tedious operations.

Gossypitrin consists of pale orange-yellow needles, melting at about 200°–202°. It is hydrolysed by boiling dilute acids into gossypetin and probably glucose, according to the following equation:—

$$C_{21}H_{20}O_{13}+H_2O = C_{15}H_{10}O_8+C_6H_{12}O_6.$$

The dyeing properties of the flowers are very different from those of gossypetin; this is due to the fact that they contain the three glucosides described above, and that there is no free colouring matter present. The following are the shades produced on mordanted woollen cloth with this material:—

Aluminium	*Tin*	*Chromium*	*Iron*
Dull yellow	Orange brown	Dull brown-yellow	Dull olive

It has not yet been determined if any special difference exists in regard to the constituents of the Indian and Egyptian varieties of the cotton flower. Both contain a glucoside of gossypetin,

but the existence in the former of quercimeritrin and isoquercitrin is at present uncertain.

A. G. P.

COTTON SEED OIL is obtained on a large scale from the seeds of the several varieties of the cotton tree, *Gossypium*. In the United States, *Gossypium hirsutum* (Linn.), 'Upland cotton,' covered with 'linters,' is extensively cultivated, whereas the plant grown in the Sea Islands and in Egypt is *G. barbadense* (Linn.). The Indian variety of cotton seed is generally assumed to be *G. neglectum* and *G. arboreum*. Up to 60 years ago, the seed not required for planting was mostly wasted, as the oil contained therein could not be refined. Cotton seed oil was first expressed in this country in the year 1847. Since then the industry has assumed such enormous dimensions that the annual import of cotton seed to this country from Egypt, the East Indies, and South America amounts to more than 600,000 tons; in addition very considerable quantities of cotton seed oil are imported from the United States, which produce almost 200,000,000 gallons of oil per annum, of which approximately 50,000,000 gallons are exported to Europe.

The seed contains, on the average:—

	Per cent.
Oil	20·0
Water	8·5
Albuminoids	20·0
Carbohydrates	32·0
Crude fibre	15·0
Ash	4·5

The proportion of oil in the seed varies considerably with the origin of the seed. Thus Egyptian seed contains up to 24 p.c. of oil; East Indian seed on the average only 18 p.c.; American 'Uplands' and Jamaica seed, 23–24 p.c.; and Brazilian and Peruvian no more than 20–21 p.c. of oil. The seeds consist on an average of 60 p.c. of kernel and 40 p.c. of husk.

A distinction must be made between seed which must be decorticated before crushing, owing to the fine 'linter,' which cannot be removed readily, and seed which is crushed in the undecorticated state. Undecorticated seeds are chiefly crushed in England, France, and Germany, from Egyptian, Bombay, and also Smyrna seeds, whereas the vast majority of the American 'Upland seed' must be decorticated before being crushed. In some European establishments Bombay seed is decorticated before crushing.

The kernels ('meats') are permeated with cells containing a deep-brown colouring matter; hence the crude cotton seed oil running from the hydraulic presses has a ruby-red to almost black colour. The depth of the colour of crude cotton oil depends, in the first instance, on the state of freshness of the seed. The American seed, which is, as a rule, crushed shortly after having been harvested, yields a crude oil of a much paler colour than that of crude oil obtained in England, France, and Germany from Egyptian seed. The palest Egyptian crude oil is obtained from fresh seed arriving in October. When the seed is stored it undergoes deterioration ('heating,' which may also occur during the voyage); hence the crude oil obtained from Egyptian seed in July and August has a very dark colour.

In the American trade three grades of crude cotton seed oil are recognised, viz. 'prime,' 'choice,' and 'off' qualities. The crude oil is refined by treatment with a dilute caustic soda solution, at a temperature not exceeding 120°F., whereby the free fatty acids are neutralised; the soap so formed falls to the bottom and carries with it the brown colouring matter, so that the supernatant oil is of a bright-yellow colour. The oil is then washed free from soap, or, in the case of a technical oil, is treated with bleaching powder, to yield the bright-yellow oil of commerce. The first qualities of cotton seed oil which are not bleached with chemicals are used as edible oils, and are consumed in enormous quantities either as such, as a cooking oil, for tinning sardines, table oil, &c., or in the manufacture of lard substitutes, under such names as salad oil, sweet nut oil, butter oil. The last-named product is chiefly used in the manufacture of margarine and compound lard.

Cotton seed oil is, at the ordinary temperature, a pale-yellow oil of characteristic, but not unpleasant, taste. At about 12°, 'stearine' deposits. This 'stearine' would interfere with the use of cotton seed oil as a table oil or salad oil; therefore the 'stearine' is removed on a large scale by cooling the oil to a low temperature, and filtering off the deposit. The filtered oil is known in commerce as 'winter oil' ('demargarinated cotton seed oil'). According to the requirements of the market, it will not 'cloud' at 40°F. or 32°F., or even at 28°F. The sp.gr. of cotton seed oil is 0·923–0·925 at 60°F. The saponification value varies from 190 to 193, and its iodine value from 105 to 115.

The solid fatty acids in cotton seed oil consist chiefly of palmitic acid; small quantities of arachidic acid seem to be present, but stearic acid appears to be absent. The liquid fatty acids would seem to consist of oleic and linolic acids only.

Cotton seed oil eminently typifies a semi-drying oil. In the Livache test (*see* OILS AND FATS) it absorbs 5·9 p.c. of oxygen in 24 hours. By blowing air through cotton seed oil at a temperature of about 90°–100°, oxygen is absorbed, with the formation of a small amount of oxidised acids, the acetyl value of the oil rising at the same time considerably. This reaction is used on a large scale in the preparation of 'Blown Cotton Seed Oil' (see OILS AND FATS), which is used in considerable quantities as a lubricating oil in admixture with mineral oils, to produce the 'Marine Lubricating Oils' of commerce.

A reliable test for the identification of cotton seed oil, and for the detection of it in other oils and fats, down to even 1 p.c. (under favourable circumstances), is the *Halphen* colour test, which is carried out in the following manner: 1–3 c.c. of the oil is dissolved in an equal volume of amyl alcohol; to this is added 1–3 c.c. of carbon disulphide, holding in solution 1 p.c. of sulphur flowers. The test-tube is immersed in boiling water, or, better, in boiling brine, the carbon disulphide being allowed to evaporate off. In the course of 5–20 minutes, a deep-red colouration appears, the intensity of which stands in direct proportion to the amount of cotton seed oil in the sample. Although the test cannot be used as a quantitative one, yet it must be considered, if positive, as one of the

best means of recognising the presence of cotton seed oil qualitatively. A negative Halphen test is, however, no conclusive proof of the absence of cotton seed oil in a mixture, as the colouring matter is destroyed by heating cotton seed oil to 250°, or by keeping it at 200° for some prolonged time, or by 'blowing' it. Hence 'blown cotton seed oils' do not show the Halphen colour reaction. J. L.

COUMARIN $C_9H_6O_2=C_6H_4\begin{cases}CH:CH\\ |\\ O—CO\end{cases}$ (1, 2) was obtained by Vogel (Gilb. Ann. 64, 161), in 1820, from the tonka bean (the seed of *Dipteryx* (*Coumarouna*) *odorata*, Willd.), or from the melilot (*Melilotus officinalis*, Lam.), and from the woodruff (*Asperula odorata*, Linn.), but was mistaken by him for benzoic acid. Guibort, however, showed that the crystalline odoriferous principle of the tonka bean was distinct from benzoic acid, and named it *coumarin*. It occurs in *Peristrophe angustifolia* (Nees), *Achylis triphylla* (DC.), and in many other plants, and is a normal constituent of lavender oil. It is present in plants as a glucoside, which is decomposed by a ferment present in the plant. This ferment is destroyed by alcohol or boiling water (Molish, J. Pharm. Chim. 1902, 279).

It was first obtained synthetically by Perkin by heating the sodium compound of salicylaldehyde with acetic anhydride (Chem. Soc. Trans. 1868, 53); or more simply by boiling together salicylaldehyde, acetic anhydride, and dry sodium acetate (*ibid.* 1887, 388; see also Tiemann and Herzfeld, Ber. 1877, 284). Acetyl coumaric acid is first formed:

$$C_6H_4\begin{cases}CHO\\OH\end{cases}+\begin{matrix}CH_3\cdot CO\\CH_3\cdot CO\end{matrix}\!\!>O=C_6H_4\begin{cases}CH:CH\cdot COOH\\O\cdot CO\cdot CH_3\end{cases}+H_2O$$

which then parts with acetic acid, yielding coumarin:

$$C_6H_4\begin{cases}CH:CH\cdot COOH\\O\cdot CO\cdot CH_3\end{cases}=C_6H_4\begin{cases}CH:CH\\ |\\ O—CO\end{cases}+CH_3\cdot COOH.$$

By treating salicylaldehyde (1 molecule) with excess of acetic anhydride (4 molecules) for 6 hours at 180°, coumarin is formed (Reychler, Bull. Soc. chim. 1897, 17, 517).

Coumarin is also formed in small quantity by heating a mixture of phenol and malic acid with sulphuric acid:

$$C_6H_5\cdot OH+\begin{matrix}CH_2COOH\\ |\\ CH(OH)\cdot COOH\end{matrix}=C_6H_4\begin{cases}CH:CH\\ |\\ O—CO\end{cases}+CO+3H_2O$$

(Von Pechmann, Ber. 1883, 2119; 1884, 929, 1649).

Substituted coumarins may be obtained by condensing phenols with acetoacetic ester or with malic acid in the presence of concentrated sulphuric acid.

Coumarin forms rhombic crystals melting at 67°; boils at 290°-290·5°; has a pleasant, aromatic odour; is scarcely soluble in cold water, readily soluble in boiling water, very soluble in alcohol and ether. Crude coumarin may be purified by repeated boiling with light petroleum (Claassen, Pharm. J. 1897, 161).

It dissolves in caustic alkalis, and is reprecipitated on addition of acids. If, however, it is heated for some time with concentrated caustic alkali, or better, with sodium ethoxide, a solution is formed from which acids precipitate coumaric acid $C_6H_4\begin{cases}CH:CH\cdot COOH\\OH\end{cases}$ (1, 2). This compound can be reconverted into coumarin by heating it with acetic anhydride; but when heated alone it is decomposed, yielding phenol and other substances. Reduction of coumarin with zinc in alkaline solution or sodium amalgam in aqueous solution yields melilotic acid as the chief product; with sodium amalgam, and alcohol hydrocoumaric acid is formed (Williamson, J. 1876, 587).

In Germany, woodruff (Ger. *Waldmeister*) is steeped in white wine, to which it imparts the pleasant aroma of coumarin (*Maiwein, Maitrank*). Instead of woodruff, an alcoholic solution of coumarin is employed for the same purpose under the name of *Maiweinessenz*. In larger doses coumarin is stated to have a narcotic action.

Coumarin has the agreeable odour of asperula, and is used in perfumery for the preparation of asperula essence. It is also frequently used to adulterate extract of vanilla (*q.v.*) (*v.* LACTONES).

COUMARONE $C_6H_4\begin{cases}CH\\ \\O\end{cases}\!\!>CH$. An oil obtained from the coal-tar fraction boiling between 165° and 175°. After the pyridine bases and phenols have been removed by acid and alkali, it is obtained as the dibromide on addition of bromine. The dibromide is reduced to coumarone by alcoholic potash and sodium amalgam (Kraemer and Spilker, Ber. 1890, 78). It can also be obtained from this source by adding picric acid to the mixture of oils, whereby the picrate of coumarone crystallises out. This is separated, decomposed by hot water or dilute alkali, and the coumarone obtained by steam distillation. The picric acid is recovered and used for another operation (Ch. Fab. Act. ges. Hamburg, Eng. Pat. 1422; D. R. P. 53793; Ber. 1891, Ref. 233). Coumarone has been synthesised by heating *o*-hydroxy-ω-chlorcinnamene $OH\cdot C_6H_4\cdot CH:CHCl$ with potash, hydrogen chloride being eliminated (Komppa, Ber. 1893, 2968). It has also been prepared by heating phenoxyacetaldehyde with zinc chloride in glacial acetic acid (Stoermer, *ibid.* 1897, 1700).

Coumarone boils at 174·0° (corr.) (Perkin, Chem. Soc. Trans. 1896, 1249). It is unacted upon by potash or by hydrochloric acid. Sulphuric acid reacts with coumarone in benzene solution, producing a soluble resinous material paracoumarone $(C_8H_6O)_4$, which is used to preserve wood and paper. Other polymerides are known. Coumarone is of interest as, when passed through a red-hot tube with benzene, phenanthrene is produced, and with naphthalene, chrysene is produced (Kraemer and Spilker, Ber. 1890, 84). The methyl coumarones are present in the coal-tar fraction of b.p. 185°-195° (Stoermer and Boes, *ibid.* 1900, 3013).

COUPIER'S BLUE *v.* INDULINES

COVELLITE. Native cupric sulphide CuS, crystallising in the hexagonal system. Crystals

are rare and have the form of thin six sided plates. The mineral has a characteristic indigo-blue colour, hence the name *indigo-copper* (German, *Kupferindig*). It occurs in most copper-mines as a blue, earthy coating on other sulphide ores of copper, and is sometimes found in sufficient quantities to be of importance as an ore, *e.g.* at Butte in Montana, and Copiapo in Chile. Covellite containing platinum (as the mineral sperrylite, $PtAs_2$) is mined in the Medicine Bow Mountains in Wyoming.

L. J. S.

COW TREE WAX *v.* WAXES.

CRANBERRY, the fruit of *Vaccinium Oxycoccos* (Linn.).

American analyses give as the average composition of the berries:

Water	Protein	Fat	Carbohydrates	Ash
88·5	0·5	0·7	10·1	0·2

König gives:

Water	Protein	Free acid	Sugar	Other carbohydrates	Ash
89·6	0·12	2·3	1·5	6·3	0·15

The juice of cranberries was examined by Mach and Portele in 1888 (Landw. Versuchs. Stat. 1889, 38, 69), who found a litre of the fresh juice to contain (in grammes)

Invert sugar	Acidity (as malic acid)	Benzoic acid	Tannic acid	Ash	Nitrogen
87·1	19·0	0·75	2·2	3·0	0·11

The sp.gr. of the juice averaged 1·0591.

The juice will not ferment with yeast, owing, it is said, to the presence of benzoic acid, but this may be due to the poverty of the juice in nitrogenous matter, for Otto (Bied. Zentr. 1899, 28, 284) found that bilberry juice would only ferment vigorously with yeast after the addition of asparagine (about 0·6 gram per litre) or of ammonium chloride (about 0·3 gram per litre).

Claassen (*ibid.* 16, 70) isolated a bitter substance from cranberries, to which he gave the name *oxycoccin*, and which he found to give reactions similar to those of arbutin $C_{12}H_{16}O_7$, occurring in the leaves of the red bearberry, *Arctostaphylos Uva-ursi* (Spreng.).

The ash of cranberry juice contains about 3 p.c. of phosphorus pentoxide and 47 p.c. of potash. H. I.

CREAM OF TARTAR *v.* TARTARIC ACID.

CREATINE, *Methylglycocyamine*, *Methylguaninoacetic acid* $H_2N{\cdot}C(NH)NMe{\cdot}CH_2{\cdot}CO_2H,H_2O$ discovered by Chevreul (Annalen, 1835, 4, 293) in muscular flesh (κρέας=flesh), occurs in human flesh and in the flesh of many warm and cold blooded animals (Liebig, Annalen, 1847, 62, 257; Gregory, *ibid.* 1848, 64, 105; Schlossberger, *ibid.* 1848, 66, 80; Voit, Z. Biol. 1868, 4, 77; Price, Chem. Soc. Trans. 1851, 3; Marcet, *ibid.* 1864, 2, 406); the amount varies with the species, the flesh of fowl yields 3·21 p.c.; of pigeon, 0·825 p.c.; of ox, 0·697 p.c.; of ox heart, 1·375 p.c.; of herring, 1·324 p.c.; and of brill, 0·614 p.c. (Gregory, *l.c.*).

According to Folin (Amer. J. Physiol. 1905, 13, 45, 66, 117), van Hoogenhuyze and Verploegl (Zeitsch. physiol. Chem. 1908, 57, 161), and Mellanby (J. Physiol. 1908, 36, 447), muscular creatine has its origin in the liver. This organ is continuously forming creatinine from substances carried to it by the blood from other organs, and in the developing muscle. This is changed to creatine, until the muscle is saturated with creatine, when the excess of creatinine is excreted by the kidneys. The creatine is presumably combined with the muscular protoplasm, for though a readily dialysable substance, it does not pass into the surrounding lymph or blood *in vitro*, nor is it readily obtainable by diffusion from muscular flesh (Urano, Beitr. Chem. physiol. Path. 1907, 9, 104).

In order to extract creatine, the flesh is heated with its own weight of water at 60°, and the juice expressed. The flesh extract is then heated to coagulate the protein, and filtered; the filtrate is treated with basic lead acetate until no further precipitation occurs, and again filtered after removing the excess of lead from the filtrate by sulphuretted hydrogen, when it is evaporated until creatine separates on cooling; this is washed with alcohol and recrystallised from water (Neubauer, Zeitsch. anal. Chem. 1863, 2, 26; 1867, 6, 33).

Creatine is prepared synthetically by heating sarcosine with cyanamide at 100°.

$$CN{\cdot}NH_2+NHMe{\cdot}CH_2{\cdot}CO_2H \rightleftharpoons NH:C(NH_2){\cdot}NMe{\cdot}CH_2{\cdot}CO_2H$$

(Volhard, Z. Chem. N. F. 1869, 5, 318; Strecker, J. 1868, 686); or, together with creatinine, by fusing sarcosine with guanidine carbonate (Paulmann, Beilstein Suppl. i. 657).

Creatine forms colourless transparent monoclinic prisms, containing $1H_2O$, which it loses at 100°; it dissolves in 74·4 parts of water at 18°; or in 9810 parts of cold absolute alcohol, and is insoluble in ether (Liebig, Annalen, 1847, 62, 257). The presence of urea, creatinine, or certain salts, raises the solubility of creatine in water and alcohol (Neubauer, *l.c.*). The aqueous solution is neutral, and has a bitter, harsh taste.

Creatine is decomposed by boiling baryta water into sarcosine, urea, and methylhydantoïn

$$NH:C(NH_2){\cdot}NMe{\cdot}CH_2{\cdot}CO_2H+H_2O = CO(NH_2)_2+NHMe{\cdot}CH_2{\cdot}CO_2H$$

$$CO(NH_2)_2+NHMe{\cdot}CH_2{\cdot}CO_2H \rightarrow CO\begin{cases}NMe{\cdot}CH_2\\ |\\ NH\cdot CO\end{cases}$$

(Neubauer, Annalen, 1866, 137, 294); or by mercuric oxide and water into oxalic acid and methylguanidine; or by heating with soda lime into ammonia and methylamine. When potassium hydroxide is added to an aqueous solution of creatine and silver nitrate until the white precipitate first formed just redissolves, the liquid solidifies to a transparent gelatinous mass immediately reduced on heating, or in the course of a few hours at the ordinary temperature. The addition of potassium hydroxide to a solution of creatine and mercuric chloride precipitates a white crystalline compound $(C_4H_9O_2N_3)_2Hg,HgO$ (Engel, Compt. rend. 1874, 78, 1707; 1875, 80, 885). Creatine is converted into creatinine by heating with dilute mineral acids for some hours (Dessaignes, J. 1857, 544), or at 117° for 15 minutes (Benedict and Myers, Amer. J. Physiol. 1907, 18, 362); or by heating with water only in sealed tubes at 100° for 2-3 days (Neubauer, Zeitsch. anal. Chem. 1863, 2, 33).

Creatine forms soluble normal salts with the mineral acids (Dessaignes, Annalen, 92, 409), and readily soluble compounds with zinc chloride $C_4H_9O_2N_3,ZnCl_2$; and cadmium chloride

$C_7H_9O_2N_3,CdCl_2,2H_2O$ (Neubauer, *ibid.* 137, 300).

Creatine cannot be estimated directly; it is usually converted into creatinine (*q.v.*), and estimated as such.

α-Guaninopropionic acid, alacreatine

$NH_2{\cdot}C(NH)NH{\cdot}CHMe{\cdot}CO_2H$

from alanine and cyanamide (Baumann, Annalen, 1873, 167, 83), an isomeride of creatine forms, sparingly soluble prisms.

The homologues of creatine are prepared by the action of cyanamide on the corresponding amino-acid in the presence of ammonia, *e.g.* *α-aminocaprocyamine*

$NH_2{\cdot}C(NH)NH{\cdot}CH(CO_2H)CH_2{\cdot}CHMe_2$

from leucine and cyanamide (Duvillier, Compt. rend. 1886, 103, 211; 1887, 104, 1290). According to Duvillier (*l.c.*) methyl- or ethylamino-acids yield with cyanamide the corresponding *creatinine*. The *creatine* is formed only in the case of methylglycocine and β-methylaminopropionic acid, the latter yielding *methylalacreatine* $NH_2{\cdot}C(NH){\cdot}NMe{\cdot}CHMe{\cdot}CO_2H$ (Lindenberg, J. pr. Chem. 1875, [2] 12, 253). This generalisation is not confirmed by Gansser (Zeitsch. physiol. Chem. 1909, 61, 16), who obtained the creatinine and not the creatine from α-methylaminopropionic acid and cyanamide, but prepared *β-methylguaninopropionic acid* $NH_2{\cdot}C(NH)NMe{\cdot}[CH_2]_2CO_2H,H_2O$, m.p. 201°–202°, from cyanamide and β-methylaminopropionic acid, and *γ-methylguaninobutyric acid* $NH_2{\cdot}C(NH)NMe{\cdot}[CH_2]_3CO_2H$, m.p. 307°, from cyanamide and γ-methylaminobutyric acid.

Formaldehyde and creatine yield the *compound* $C_6H_{11}O_3N_3,2H_2O$, decomposing at 250°, and forming a *dibenzoyl-derivative* $C_6H_9O_3N_3Bz_2$, m.p. 265°–266° (Jaffé, Ber. 1902, 35, 2896).

Phthalyldicreatine

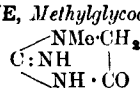
$C_6H_4[CO{\cdot}NH{\cdot}C(NH){\cdot}NMe{\cdot}CH_2{\cdot}CO_2H]_2$

has m.p. 212° (Urano, Beit. Chem. Physiol. Path. 1907, 9, 183). *Diacetylcreatine*

$NH:C(NHAc)NMe{\cdot}CH_2{\cdot}CO_2Ac$

has m.p. 165° (Erlenmeyer, Annalen, 1895, 284, 50). M. A. W.

CREATININE, *Methylglycocyamidine*

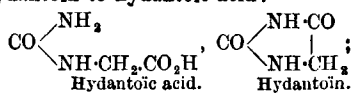


discovered by Liebig in human urine (Annalen, 1847, 62, 268), the amount excreted being 26–30 mg. per kilo. weight of body per diem (Koch, Amer. J. Physiol. 1905, 15, 1), is also a constant constituent of the urine of horses, cows, dogs, pigs, and rabbits; it occurs in small quantities in the flesh of fish, about 0·2 p.c. in the case of cod (Poulsson, Chem. Zentr. 1904, ii. 30); and traces (0·000098 p.c.) are found in blood (Cooper Colls, J. Physiol. 1896, 20, 107).

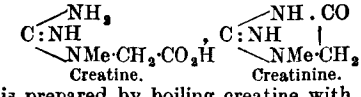
Under normal conditions, the excretion of creatinine is constant from day to day and hour to hour (Shaffer, Amer. J. Physiol. 1908, 23, 1); it is not affected by diet or exercise (Folin, *ibid.* 1905, 13, 45, 66, 117; Pekelharing, van Hoogenhuyze Verploegh. Proc. k. Akad. Wetensch, Amsterdam, 1905, 8, 363; Klercker, Beit. Chem. Physiol. Path. 1906, 8, 59). It is now generally regarded as one of the end products of endogenous nitrogenous katabolism, the liver continuously forming creatinine from substances carried to it by the blood; part of this creatinine furnishes the muscular creatine by the change it undergoes in the developing muscle; the rest is excreted by the kidneys (Folin, *l.c.*; Mellanby, J. Physiol. 1908, 36, 447; Lefmann, Zeitsch. physiol. Chem. 1908, 57, 476). In cases of fever or starvation, the amount of urinary creatinine is increased, the material wanted for contraction being drawn from the muscular proteids (Pekelharing, van Hoogenhuyze Verploegh, *l.c.*: Leathes, J. Physiol. 1907, 35, 205). In cancer of the liver, the urinary creatinine is diminished and the creatine is increased (Mellanby, *loc. cit.*).

Creatinine is extracted from urine by evaporating to one-third the original volume, decanting from the salts that crystallise out, precipitating with lead acetate and filtering, removing the lead from the filtrate and precipitating the creatinine as the sparingly soluble double salt with mercuric chloride. This is separated, decomposed by sulphuretted hydrogen, and the creatinine crystallised from the filtrate as the hydrochloride (Maly, Annalen, 1871, 159, 279).

Creatinine bears the same relation to creatine as hydantoïn to hydantoïc acid:



Hydantoïc acid. Hydantoïn.



Creatine. Creatinine.

and is prepared by boiling creatine with dilute mineral acids for some hours (Liebig, Annalen, 1847, 62, 628) or by heating at 117° for 15 minutes under pressure (Benedict and Myers, Amer. J. Physiol. 1907, 18, 362).

Creatinine can be prepared synthetically by heating guanidine carbonate with sarcosine at 140°–160° (Horbaczewski, J. Pharm. Chim. 1885, 86).

Creatinine forms anhydrous monoclinic prisms soluble in 11·5 parts of water or 100 parts of absolute alcohol at 16° (Liebig, *l.c.*), and separates on slow evaporation of dilute solutions in square plates containing $2H_2O$ (Salkowski, Zeitsch. physikal. Chem. 1880, 4, 133). It is a weak base, displacing ammonia from its salts, and forming soluble salts with the mineral acids (Liebig, *l.c.*), the *picrate* $C_4H_7ON_3{\cdot}C_6H_3O_7N_3$, m.p. 212°–213°, crystallises in sparingly soluble yellow needles; the *acid picrate*

$C_4H_7ON_3{\cdot}2C_6H_3O_7N_3$

has m.p. 161°–166° (Mayerhoffer, Wien. Klin. Woch. 1909, 22, [3]); the *tartrate*

$(C_4H_7ON_3)_2{\cdot}C_4H_6O_6$

decomposes at 207°–209°; the *oxalate*

$(C_4H_7ON_3)_2{\cdot}C_2H_2O_4$

is sparingly soluble in alcohol (Poulsson, Chem. Zentr. 1904, ii. 30). Creatinine forms characteristic double salts with platinic chloride $(C_4H_7ON_3,HCl)_2{\cdot}PtCl_4$, orange-red plates, m.p. 220°–225°; with auric chloride

$C_4H_7ON_3{\cdot}HCl{\cdot}AuCl_3$;

yellow crystals, m.p. 170°–174°; with potassium picrate $C_4H_7ON_3{\cdot}C_6H_3O_7N_3{\cdot}KC_6H_2O_7N_3$, lemon-yellow prisms, 100 parts of water dissolve 0·1806 part of the salt at 19°–20°; with zinc chloride

$(C_4H_7ON_3)_2{\cdot}ZnCl_2$, almost insoluble in alcohol (Heintz, J. 1847, 48, 883); with mercuric chloride $4(C_4H_8HgON_3{\cdot}HCl){\cdot}3HgCl_2,2H_2O$ (Johnson, Proc. Roy. Soc. 1886, 43, 493).

Creatinine is converted into creatine by the action of cold dilute ammonia or calcium hydroxide solutions; boiling baryta solution converts it into ammonia and methyl hydantoïn; with alkaline oxidising agents it yields methylguanidine and oxalic acid, but is comparatively stable towards acid permanganate solutions (Jolles, Ber. 1902, 35, 160).

The presence of creatinine in dilute solution or in urine can be detected by (1) Maschke's test (Zeitsch. anal. Chem. 1878, 134), which consists in the formation of a sparingly soluble double compound of creatinine and cuprous oxide, when the suspected solution is heated at 50°–60° with Fehling's solution; as the cuprous oxide is formed by the oxidation of part of the creatinine, it is advisable to add a little glucose to the mixture; the test is sufficiently delicate to allow of the detection of $\frac{1}{10000}$ part of creatinine. (2) Weyl's test (Ber. 1878, 11, 2175) consists in the production of a ruby-red colouration, changing to yellow when, to a solution of creatinine, a few drops of 10 p.c. sodium nitroprusside and the same quantity of 10 p.c. sodium hydroxide or carbonate solution are added. On acidifying the solution with acetic acid and boiling, the colour becomes emerald green, changing to blue, due to the formation of Prussian blue (Salkowski; Colasanti, Gazz. chim. ital. 1887, 17, 129). Guareschi (Ber. 1888, 21, Ref. 372) has shown that this reaction is given by other compounds than creatinine containing the $-CO{\cdot}CH_2-$ complex. (3) Jaffe's test (Zeitsch. physiol. Chem. 1886, 10, 399) is the production of a deep-red colour, when picric acid and an excess of sodium hydroxide solution are added to the liquid containing the creatinine. Chapman (Chem. News, 1909, 100, 175) has shown that the colour is due to the sodium salts of aminodinitrophenol (picramic acid), and diaminonitrophenol formed by the reduction of the picric acid by the creatinine; if the creatinine is present in excess, reduction to the colourless triaminophenol occurs.

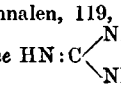
The older methods for the estimation of creatinine were based upon the isolation of the base in the form of its sparingly soluble double salt with mercuric or zinc chloride, and either weighing the precipitate or estimating the metal or the nitrogen in the compound (Neubauer, Annalen, 119, 35; Salkowski, Zeitsch. physiol. Chem. 1886, 10, 113; Grocco, Chem. Zentr. 1887, 17; Kolisch, *ibid.* 1895, i. 814; Ladd and Bottenfield, Amer. Chem. J. 1898, 20, 869; Edleson, Chem. Zentr. 1909, i. 108) recommends precipitating the sulphate in the presence of alcohol and ether, dissolving it in water, and titrating the solution with standard barium hydroxide solution, using phenol phthalein as indicator.

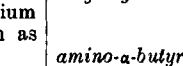
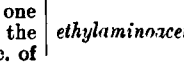
The method generally adopted for estimating creatinine in urine is Folin's colorimetric method, based on Jaffe's reaction (Zeitsch. physiol. Chem. 1904, 41, 223). N/2 potassium dichromate solution is placed to a height of 8 mm. in one tube of a Duboscq colorimeter; 100 c.c. of the urine is placed in a 500 c.c. flask with 10 c.c. of a 1·2 p.c. solution of picric acid and 5 c.c. of a 10 p.c. solution of sodium hydroxide, left for a few minutes and made up to the mark. If x is the length of this solution in the second tube required to give the same colour effect as the 8 mm. of the standard dichromate solution in the first tube, then $8{\cdot}1\times10/x$=mg. of creatinine in the 10 c.c. of the urine. If x is less than 5, only 5 c.c. of urine should be used; if x is greater than 13, then 20 c.c. of urine should be used. If creatine is also present in the urine, the amount may be estimated by first determining the creatinine as above, then converting the creatine in another 10 c.c. of the urine to creatinine by heating it with 5 c.c. of N/2 HCl on the water-bath for 3 hours or for 15 minutes at 117° under pressure (Benedict and Myers, Amer. J. Phys. 1907, 18, 362), and estimating the total creatinine. The difference between the two results represents the amount of creatinine equivalent to the creatine originally present. (For precautions to be observed regarding temperature, time, and dilution, in applying this method for the estimation of creatinine, compare Chapman, Chem. News, 1909, 100, 175.)

Two isomeric *nitrosocreatinines* were obtained by Dessaignes (Annalen, 1856, 97, 341) and Märcker (*ibid.* 1865, 133, 305) by passing the nitrous fumes from the action of nitric acid on arsenious oxide into an acid solution of creatinine. The less soluble *α-nitrosocreatinine* $C_4H_8O_2N_4$ decomposes at 210°, forming a colourless liquid that quickly solidifies to a brown mass from which a new *base* $C_7H_{12}O_2N_{10}$ (?) can be extracted; it forms a crystalline *nitrate*, *hydrochloride*, and *platinichloride*, and yields the *bromoderivative* $C_4H_7O_2N_4Br$. The more soluble *β-nitrosocreatinine* $C_4H_8O_2N_4$ melts at 195° to a brown liquid and decomposes at 220°.

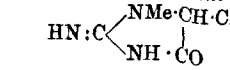
According to Kramm (Chem. Zentr. 1898, i. 37), the yellow colour formed by the interaction of sodium nitroprusside and sodium hydroxide on creatinine (*cf.* Weyl, Ber. 1878, 11, 2175), is due to the formation of a *nitrosocreatinine* $C_4H_6O_2N_4$, which can be isolated as a colourless crystalline precipitate by adding acetic acid to the yellow alkaline solution and shaking vigorously.

The following *acyl-* and *alkyl-* derivatives of creatinine have been prepared: *Benzoylcreatinine* $C_{11}H_{11}O_2N_3$, pale yellow needles, m.p. 187° (Urano, Beitr. Chem. Physiol. Path. 1907, 9, 183); *methylcreatinine* $C_5H_9ON_3,H_2O$ and its salts and platinichloride (Korndörfer, Arch. Pharm. 1904, 242, 641); *ethylcreatinine*



(Neubauer, Annalen, 119, 50); *methylamino-α-butyrocyamidine*  ; *ethylamino-α-butyrocyamidine* ; *ethylaminopropionocyamidine*  ; *ethylaminoacetocyamidine* ;

methylaminoisovalerocyamidine



α-aminocaprocyamidine

(Duvillier, Compt. rend. 1882, 95, 456; 96, 1583; 97, 1486; 100, 916; 103, 211; 104, 1290).—For *Xantho-*, *Cruso-* and *Amphi-creatinine* v. *Xanthocreatinine*. M. A. W.

CREOLIN. A disinfectant consisting of a mixture of coal tar with colophony or Venetian turpentine, in a caustic soda solution.

CREOSOTAL (*Creosote carbonate*) is a mixture of carbonates of the phenols present in wood creosote, of which the chief are guaiacol and creosol.

It is produced by heating creosote with a benzene solution of carbonyl chloride (phosgene) under pressure (Heyden, Eng. Pat. 19074, 1890), but is generally prepared by passing phosgene gas through a solution of beech-wood creosote in caustic soda solution. The carbonate separates as an oil, and is washed with dilute caustic soda and finally with water.

Creosotal is a viscid yellowish liquid, insoluble in water, but soluble in alcohol, chloroform, benzene, &c. (Aufrecht, Pharm. Zeit. 1908, 53, 480). When it is boiled with caustic potash, the odour of creosote is evolved. It is quite odourless, tasteless, and non-irritant in its action upon the mucous membrane, and is therefore much used as a substitute for creosote in the treatment of bronchial affections and pneumonia, especially in children (Weber, Pharm. J. 68, 115; Toff, *ibid.* 73, 414). The dose for adults is about 60 grains daily, and it is usually given in an emulsion (Haefelin, Pharm. Zeit. 49, 141).

CREOSOTE or **KREOSOTE** (from *κρέως*, contracted genitive of *κρέας*, meat, and *σωζώ*, I save or preserve). Wood tar, and coal tar, when subjected to distillation, yield fractions technically known as 'creosote,' both of which, the latter more especially, find extensive and important uses in the industrial arts.

Reichenbach, in the year 1832, applied the term 'kreosote' to a substance derived from wood tar, and which has been found to possess powerful antiseptic properties; shortly afterwards, Runge discovered carbolic acid in coal tar, and the two products were, for a considerable time, regarded as identical; similar compounds, however, have since been procured from other sources, and in order to prevent confusion, it has been suggested to restrict the use of the term 'creosote' to the use in a generic sense as referring to all the phenols and phenoloid bodies derived indifferently from coal, wood, coke-oven, blast-furnace, and shale-oil tars. The enormous extension of the use of creosote oil from coal tar for the preservation of timber has resulted in the terms 'creosote' and 'creosote oil' being used commercially as meaning the heavier distillates from coal tar and coke oven-tar, the oils from blast-furnace tar being distinguished as 'blast-furnace creosote.'

Wood-tar creosote. The tar derived from the distillation of beechwood, when subjected to further distillation, yields certain fractions that are heavier than water, and which, after agitation with solution of caustic soda, and separation from insoluble oils, are boiled with free access of air in order to oxidise various impurities present; the alkaline solution thus obtained is decomposed with dilute sulphuric acid, the crude creosote which separates is again submitted to a similar alkaline and acid treatment, and the product finally distilled, reserving the fraction passing over between 200° and 220°.

This represents the ordinary 'wood-tar creosote' of commerce. It is a complex mixture of phenoloid compounds, the proportions of which are materially influenced by the method originally followed in distilling the beechwood from which it was obtained.

Wood-tar creosote, when freshly prepared, is a colourless, transparent liquid of an oily consistency, and which retains its fluidity at a very low temperature; its sp.gr. varies from 1·037 to 1·087; it boils at 205°–225°, and dissolves in about 200 parts of water; its odour is strong and penetrating, resembling that of wood smoke, or rather of smoked meat; it refracts light powerfully and burns with a very sooty flame. Wood-tar creosote is powerfully antiseptic, but its power of coagulating albumen has been denied; nevertheless, it preserves animal substances as effectively as carbolic acid. It is less caustic than carbolic acid, and is not poisonous. Wood-tar creosote may be regarded as consisting of a mixture of compounds included in several homologous series, chiefly of acid methylic ethers of catechol, and the presence of the following bodies has been established:—

Name	Formula	Boiling-point
1. Monohydric phenols:		
Phenol, carbolic acid	C_6H_5OH	182°
Cresols, cresylic acid (1–2, 1–3, 1–4)	$C_6H_4(CH_3)OH$	203°
Xylenols or phlorols (1–3–4, 1–3–5)	$C_6H_3(CH_3)_2OH$	220°
Ethyl-phenol (1–2)	$C_6H_4(C_2H_5)OH$	203°
2. Methyl ethers of dihydric phenols:		
Guaiacol or methyl-catechol	$C_6H_4\{OCH_3\}\{OH\}$	200°
Creosol or methyl-homocatechol	$C_6H_3(CH_3)\{OCH_3\}\{OH\}$	219°
Dimethyl-homocatechol	$C_6H_3(CH_3)(OCH_3)_2$	214°–218°
Homocreosol or dimethyl-guaiacol	$C_6H_2(CH_3)_2\{OCH_3\}\{OH\}$	230°
Ethyl-guaiacol (1–3–4)	$C_6H_3(C_2H_5)\{OCH_3\}\{OH\}$	—
Cœrulignol or propyl-guaiacol	$C_6H_3(C_3H_7)\{OCH_3\}\{OH\}$	241°
3. Methyl ethers of trihydric phenols:		
Dimethyl-pyrogallol	$C_6H_3\{OCH_3\}\{OCH_3\}\{OH\}$	253°
Dimethyl-methyl-pyrogallol	$C_6H_2(CH_3)\{OCH_3\}\{OCH_3\}\{OH\}$	265°
Dimethyl-propyl-pyrogallol (picamar)	$C_6H_2(C_3H_7)\{OCH_3\}\{OCH_3\}\{OH\}$	285°
Methyl-propyl-pyrogallol	$C_6H_2(C_3H_7)\{OCH\}\{OH\}\{OH\}$	290°

Of these compounds, phenol is present in extremely small quantity, paracreosol in larger, and phlorol in notable proportion, but the two principal constituents of creosote are guaiacol and creosol, although not equally present in all varieties; guaiacol, according to Allen, predominates in Rhenish creosote, whilst with Morson's creosote from 'Stockholm tar,' creosol

is the chief constituent. Homocreosol and cœrulignol are present in small quantity only, but, according to Grätzel, the latter body possesses such energetic and astringent qualities that a single drop placed on the tongue causes bleeding; purified creosote should therefore be absolutely free from this compound, which may be detected by the blue colouration produced by barium hydroxide.

The less valuable portions of wood-tar creosote have been found by A. W. Hofmann to contain the methyl ethers of pyrogallol and its homologues; these bodies are of interest from the remarkable colouring matters (originally discovered by Runge) which may be derived from them by oxidation; thus, if the sodium derivative of dimethyl-pyrogallol be mixed with the sodium derivative of dimethyl-methyl-pyrogallol and excess of sodium hydroxide and heated in the air, a substance called eupittonic acid is formed, according to the following equation:—

$$(C_8H_{10}O_3)_2+C_9H_{12}O_2+2O_2=C_{45}H_{26}O_9+3H_2O.$$

Eupittonic acid has the constitution of a hexamethoxyl aurin $C_{19}H_8(OCH_3)_6O_3$. Reichenbach's 'pittical,' called by Wichelhaus 'eupittone,' was a salt of eupittonic acid. Wood-tar creosote has been met with adulterated to a considerable extent with crude carbolic and cresylic acids, and from the fact that the reactions of these substances closely resemble those of wood creosote, the distinction between the two, especially when in admixture, is attended with some difficulty. Genuine beechwood tar is soluble in solutions of caustic alkalis, and forms a crystalline compound with potassium hydroxide, but not with sodium hydroxide; on the other hand, it is practically insoluble in strong ammonia.

An alcoholic solution should give no colouration whatever (blue or red) with baryta water; such colouring indicates the presence of cœrulignol and other impurities.

The composition of beechwood and oak creosotes, freed from hydrocarbons, is given by Béhal and Choay (Compt. rend. 1894, 119, 166), as follows:—

	Beech	Beech	Oak
Distillation temperature, °C.	200–220°	200–210°	200–210°
Specific gravity	1·085	1·085	1·068
Monophenols	39·0	39·0	55·0
Guaiacol	19·7	26 5	14·0
Creosols and homologues	40·0	32·1	31·0
Loss	1·3	2·4	—

Owing to the demand for guaiacol for pharmaceutical purposes, wood-tar creosote, as it occurs in commerce, is frequently found to have been deprived of part or the whole of the guaiacol it contained.

Methods for the determination of guaiacol in wood creosote are given by Béhal and Choay (Compt. rend. 1893, 116, 197); M. Adrian (Nouv. Rem. 13, 97); L. F. Kebler (Amer. J. Pharm. 1899, 409).

Wood-tar creosote is sharply distinguished from the coal-tar acids by its insolubility in absolute glycerol; it is also distinguished from the coal-tar acids by its reaction with an ethereal solution of nitrocellulose; shaken with half its volume of collodion, B.P., Calvert's No. 5 carbolic acid coagulates the gun-cotton. Morson's creosote does not precipitate the nitrocellulose from collodion, but mixes perfectly with the ethereal solution; when a mixture of equal volumes of Morson's creosote and Calvert's No. 5 acid is treated with the collodion, the precipitation is very marked.

Coal-tar creosote, Heavy oils, Dead oils. This substance, both as regards the magnitude of its production, and the extensive uses to which it is applied, occupies a position of considerable interest and importance. As a distillate derived from coal tar, it represents the fraction passing over between 204° and 404°.

As far as can be gathered from trustworthy statistics, the annual production of creosote from gas-works and coke-oven tar in the United Kingdom amounts to about 49,000.000 gallons. The census of production gave 45,303,000 gallons in 1907, the major part of which is disposed of in the creosoting of timber, very large quantities being shipped to America in bulk in special tank steamers. Considerable amounts are also used for softening hard pitch; as liquid fuel for lighting; in the production of lampblack; as an antiseptic, and as a cattle wash for the destruction of animal parasites.

Coal-tar creosote differs considerably in appearance and character; that known as 'London make' exhibits a deep greenish shade, and is more or less fluorescent; it is highly charged with naphthalene, and is not unfrequently viscid or semi-solid at ordinary temperatures. 'Midland or country' creosote shows less fluorescence, and is both thinner and more volatile. The 'Scotch' creosotes derived from cannel coal are still thinner and proportionally more volatile, and not unfrequently lighter than water; creosote oil from London coal tar is always heavier than water; the specific gravity of the portions last distilling reaching as high as 1·10, but the mean of the mixture may be taken at 1·065, while for country make it seldom exceeds 1·05. Coal-tar creosote possesses a strong unpleasant odour, highly characteristic of the fluid, and which readily distinguishes it from all others.

Any attempt to determine the absolute composition of coal-tar creosote is attended with much difficulty, but the following substances are known to be present: naphthalene, phenanthrene, anthracene, pyrene, chrysene, carbazole, benzerythrene, and other hydrocarbons accompanying the distillation of tar.

Various phenoloid bodies are also present, consisting of carbolic and cresylic acids, with higher phenols, concerning which little is really known. Basic substances, consisting of the heavier members of the pyridine series, cryptidine, quinoline, and acridine, are also present, together with the so-called indifferent oils, fluid at ordinary temperatures, and about which still less is known. Carbolic and cresylic acids vary greatly in the proportion found; for 'London creosote' the average yield of total tar acids may be stated at 4 to 7 p.c.; while for 'country make' the quantity is often considerably higher. The bulk of the pyridine or basic bodies

contained in the coal tar passes over in distillation of the lighter oils.

Employment of creosote oil for preserving timber (*creosoting*) (*v.* WOOD PRESERVATIVES).

Employment of creosote oils for softening pitch (*v.* PITCH).

Employment of creosote oils for lighting.—Creosote oil has long been employed as a source of light in the construction of harbours and outdoor work, where smoke was of little consequence or inconvenience; but when it is wished to burn this oil to the greatest advantage and with the least possible amount of smoke and soot, it becomes necessary to employ lamps so constructed that a jet of air or steam, more or less superheated, may be introduced in such a manner as to ensure more perfect combustion. Hartmann and Lucke (D. R. P. 9195, Aug. 9, 1879) constructed a lamp specially intended for the consumption of creosote oils, in which the oil is automatically supplied to a dish-shaped receptacle, over which is placed a funnel-shaped cylinder. In the centre of the dish or receptacle receiving the oil from its attached reservoir, is placed a conical tube, reaching a little above the surface of the oil, and through which a jet of superheated or dry steam may be driven. In using the lamp, the dish or receptacle referred to is allowed to fill with oil; it is then ignited at its surface, the funnel-shaped cylinder placed over it, and steam cautiously admitted through the conical tube. It will readily be seen that the arrangement closely resembles the old 'Herapath blowpipe,' with the difference that the steam is forced through a body of combustible fluid, issuing just above its surface, in place of air forced through a body or envelope of combustible gas, and issuing at a point or position that may be called its surface.

The oil thus burns without wick or chimney, and affords a light of 180 standard candles, with an hourly consumption of a little over 2 lbs. of creosote.

An apparatus for a similar purpose has been patented by Lyle and Hannay, under the name of the 'Lucigen.' It consists of an oil tank or reservoir, fitted with a special burner at the top of a tube, which may be extended to any length; into this reservoir compressed air is introduced by an indiarubber pipe, so attached as to make the 'Lucigen' portable. On the compressed air being admitted into the oil tank or receptacle, it forces the oil up through an internal tube, and, escaping at the same time with the oil in the burner, produces a spray which is set on fire. A light of about 2000 candle-power is given by the 'Lucigen.' The flame is large, the light well diffused, and the eyes are not dazzled by it. There is little or no smoke from the flame, and the lamp burns equally well under heavy rain or spray; it requires no lantern, and has no parts which can be damaged by rough usage. In the 'Doty' and 'Wells' lights, pressure is brought to bear on the surface of the oil or creosote by means of an air pump, whereby the oil is forced through a coil surrounding the lower portion of the flame, and becomes distilled into gas.

Creosote oil has also been employed for the purpose of illuminating and heating, by direct conversion into permanent gas. A ton of creosote is capable of yielding 13,300 cubic feet of gas, with an illuminating power of 14 candles; a yield of 29,300 cubic feet may be obtained, but of 8½ candle-power only; the chief drawback to this method of utilisation is the high temperature necessary to decompose the oils, and which results in the production of low candle-power gases.

Employment of creosote as fuel.—Creosote oil is extensively used as a fuel, both for marine and stationary purposes and especially for furnaces for heating iron rods for the manufacture of bolts and rivets, and, from theoretical considerations, would appear to be eminently adapted to the purpose, 1 lb. of coal-tar creosote, when effectively burnt, being capable of evaporating 11·24 lbs. of water, a result which is considerably in excess of that obtained from coal or coke.

Various methods have been devised for burning the oil to the greatest advantage. These may be briefly summarised under the following heads:—

1. Injection into the furnace by means of compressed air with 'atomising' apparatus.
2. Injection into the furnace by means of steam with 'atomising' apparatus.
3. Feeding into the furnace by simple gravitation, alone or in combination with coke.

G. F. Dexter (Journ. Gas Lighting, June 29, 1886, 1242–1244), in a table showing the relative calorific values of certain coal-tar distillates, refers to creosote, or heavy oils, as under:

Average formula $C_{14}H_{16}$; b.p. 240° to 270° and upwards.

Proportionate weight of constituents:

Carbon . . .	0·93913
Hydrogen . . .	0·06087

Calorific value:

Carbon units . . .	497
Hydrogen units . . .	210

Employment of creosote oil as an antiseptic and for the purposes of a cattle wash and sheep dip (*v.* DISINFECTANTS).

Creosote oil is also now largely used to absorb benzene from coke-oven gas. The gas, after the extraction of the ammonia, is passed up towers or scrubbers down which a shower of creosote oil falls. The creosote oil takes up from 3 to 4 p.c. of benzene, and this is regained by distillation with steam, the creosote being used over and over again until, by the accumulation of dirt and tar, it becomes too viscid, when it is generally run into the tar well. This fact should not be lost sight of when estimating the proportion of creosote in coke-oven tars.

The heavier portions of creosote oil are also used to absorb naphthalene from coal gas: the gas is passed through washers containing the oil. As the oil tends to abstract some of the illuminants from the gas, it is best to add to the oil before use a small proportion of benzene sufficient to saturate the oil so that no more is absorbed from the gas.

The heavier oils are also used as a rough lubricant for brick-making machinery, and for injecting into the brick kilns during the burning of the bricks to impart a superficial blue colour to them. The creosote acts as a reducing agent on the iron compounds in the clay, and the red colour is changed to blue.

A preparation of heavy creosote or anthracene oil with lime is used as a cart or axle grease.

The examination of creosote oil usually comprises the determination of the specific gravity, the percentage of tar acids, the amount of water present, the point at which it liquefies, and the distillation temperatures. The methods employed will be described in the article on WOOD PRESERVATIVES.

Creosotes from other sources (blast-furnace and shale oil).—Several creosotes of this character have been studied by Watson Smith and A. H. Allen. They have been found to differ materially from those derived from coal and wood tar, occupying an intermediate position. The waste gases issuing from blast furnaces fed with coal instead of coke, deposit a considerable quantity of tar yielding a creosote greatly resembling that furnished by gas tar; it differs, however, in having a lower specific gravity and in the character of the phenoloids obtained from it. The phenoloids from blast-furnace tar, extracted by Watson Smith, contained only 1·33 p.c. of real phenol, boiling at 182°, whereas the tar acids from Lancashire tars yielded 65 p.c. of crystallisable carbolic acid.

The fractions passing over between 210° and 230° contain phlorol and creosol, and those following at a higher temperature, viz. 360°, furnish compounds allied to the eupittonic acid obtained from wood tar.

The tar obtained from producers using bituminous coal also furnishes creosote strongly resembling that from blast-furnace tar.

The pyrogallic ethers, boiling respectively at 253°, 265°, and 285°, found by Hofmann in wood creosote, have also been separated from shale creosote. Blast-furnace creosote oil is now produced in vast quantities in Scotland, and the question of its application has received a considerable amount of attention. It is employed to a certain extent for creosoting timber, in producing the 'Lucigen' light, and as a liquid fuel. It furnishes from 20 to 35 p.c. of phenoloid substances soluble in caustic soda, as against 4 to 7 p.c. in London coal-tar creosote, and about 16 p.c. for Midland and country make. Allen and Angus, who have closely studied these bodies, have secured by patent their use as an antiseptic under the name of 'neosote,' a word signifying 'new preserver' (Eng. Pat. 11689, August 29, 1887). Experiments have shown that the substance compares favourably with carbolic acid, whilst its caustic properties, when applied to the skin, are very much less marked. When freshly prepared, the fluid is almost colourless, and bears the greatest resemblance to wood-tar creosote.

Bibliography.—Lunge's Coal Tar and Ammonia, 4th ed. 1909; and Allen's Commercial Organic Analysis, 4th ed. 1910. W. H. C.

CRESOL $C_6H_4(CH_3)OH$. The three isomeric cresols exist in coal tar (Williamson and Fairlie, Annalen, 92, 319; Ihle, J. pr. Chem. [2] 14, 442; Tiemann and Schotten, Ber. 11, 767, 783) in about the following proportions: orthocresol, 35 p.c.; metacresol, 40 p.c.; and paracresol, 25 p.c. (Schulze, *ibid.* 20, 410).

The cresols can be separated from the oily, non-crystallisable mother liquors obtained in the purification of crude phenol by fractionation and crystallisation, by dissolving them in soda lye, freeing the solution from naphthalene or other hydrocarbons by a current of steam, and then fractionally precipitating with sulphuric acid. The first fractions, owing to the greater acidity of phenol, contain chiefly cresols, and are further purified by distillation (Müller, Zeitsch. Chem. 1865, 270).

Various processes have been patented for obtaining meta- and para-cresol from crude cresol. Raschig (Eng. Pat. 18334; D. R. P. 112545; J. Soc. Chem. Ind. 1900, 37), by repeated fractionation of the crude cresol, obtains a mixture containing 60 p.c. of meta- and 40 p.c. of para-cresol. This mixture is then sulphonated by means of concentrated sulphuric acid, in which *m*-cresolsulphonic acid is easily soluble, but the *p*- compound only with great difficulty. The mixture is allowed to stand for a week, and the crystals of the *p*-sulphonic acid are removed, or a soluble sodium salt, such as the sulphate, may be added in quantity sufficient to form the sodium salt of the *p*-cresolsulphonic acid. The latter is separated from the mother liquor, which consists of *m*-cresolsulphonic acid and a little sodium sulphate. The two cresols are obtained from their respective sulphonic acids by hydrolysis with superheated steam. In another process (Raschig, Eng. Pat. 25269; J. Soc. Chem. Ind. 1900, 1099) the mixture of the two sulphonic acids is subjected to the action of superheated steam at 120°–130°, the *m*-cresolsulphonic acid alone being hydrolysed under these conditions. The *m*-cresol distils off, and on raising the temperature to 140°–160°, the *p*-sulphonic acid is hydrolysed and *p*-cresol is obtained.

According to the Chem. Fabr. Ladenburg (D. R. P. 148703; Chem. Soc. Abstr. 1904, i. 312), separation of *m*- and *p*-cresols, by partial sulphonation, is incomplete. The process recommended is to heat crude cresol with sodium hydrogen sulphate at 100°–110°, dissolve the product in water, when *p*-cresol separates out as an oily layer, the *m*-cresol alone being sulphonated. Superheated steam, at 180°, is passed in to obtain *m*-cresol, after the *p*-cresol has been separated.

Another process of the same firm (Eng. Pat. 1881; Fr. Pat. 339880; D. R. P. 152652; J. Soc. Chem. Ind. 1904, 759) consists in saturating the crude cresol with milk of lime, when the calcium salt of *m*-cresol, which is much less soluble than that of the *p*-cresol, separates out. This is filtered off, decomposed with acid, and relatively pure *m*-cresol is obtained. The crystals of the calcium salt, before decomposition with acid, may be washed with benzene to free them from the last traces of mother liquor. Reihm (D. R. P. 53307; Frdl. ii. 9) separates *m*-cresol from *p*-cresol by means of their barium salts.

Rütgers (Fr. Pat. 317512; D. R. P. 137584 and 141421; J. Soc. Chem. Ind. 1902, 1410) treats the commercial mixture with anhydrous oxalic acid or an anhydrous acid oxalate. By this means, the oxalic ester of *p*-cresol alone is formed and separates out. This ester is separated and decomposed by water into *p*-cresol and oxalic acid; the *m*-cresol is obtained from the mother liquors.

Synthetical preparation of ortho- and para-

cresol.—Pure ortho- and para-cresol can be obtained by fusing the potassium salts of the corresponding toluenesulphonic acids with alkali (Engelhardt and Latschinow, Zeitsch. Chem. 1869, 620), or by diazotising the corresponding toluidines. For this purpose the toluidine (15 parts) is dissolved in sulphuric acid of sp.gr. 1·8 (15 parts) diluted with 500 parts of water, treated with an aqueous solution of potassium nitrite (12 parts), and the product gradually heated with steam. The resulting cresol is then distilled with steam, the distillate treated with soda lye, then with sulphuric acid, and the liberated cresol extracted with ether and finally distilled in a current of carbon dioxide (Tiemann and Schrotter; Ihle (*loc. cit.*)).

Orthocresol can also be obtained from carvacrol by treatment with phosphorus pentoxide (Kekulé, Ber. 7, 1006). It is crystalline, melts at 30° (T. and S.; Ihle; Béhal and Choay, Compt. rend. 118, 1211), at 31°–31·5° (K.); boils at 188·5° (B. and C.), 188° (T. and S.) at 191° (corr.) (Perkin, Chem. Soc. Trans. 1896, 1182), is soluble to the extent of 2·5 vols. in 100 vols. of water, and on fusion with caustic potash is converted into salicylic acid. When nitrated, it yields dinitro-orthocresol (m.p. 86°–87°) (Nölting and Salis, Ber. 14, 987).

Metacresol is prepared by heating thymol (100 parts) with half its weight of phosphorus pentoxide for 10–12 hours until propylene ceases to be evolved, adding the product to 115–120 parts of fused alkali, and further heating the fused mixture for 5–10 minutes to decompose the cresyl phosphate formed. The melt is then dissolved in water, treated with ether to remove any undecomposed cresyl phosphate and other impurities, then acidified with hydrochloric acid, and the separated metacresol extracted with ether, and finally distilled in a current of carbon dioxide (E. and L.; T. and S.).

Metacresol is also prepared from naphthalene 1.3.3′-, 1.3.6-, or 1.3.8- trisulphonic acids, from analogous hydroxy- or amino-naphthalene mono- or di-sulphonic acids or from trihydroxynaphthalene; *e.g.* 1.3.3′- naphthalene trisulphonic acid together with half its weight of caustic soda and three quarters of water, is heated for 5 hours at 280°. The product is poured into water, acidified, boiled to expel sulphurous acid, and filtered: *m*-cresol separates out on cooling (Kalle & Co. Eng. Pat. 16559; D. R. P. 81484; J. Soc. Chem. Ind. 1895, 1800). It is ordinarily a liquid, but has been obtained in crystals, melting at 3°–4° (Städel, Ber. 18, 3443; B. and C.); it boils at 200° (B. and C.), 201° (Oppenheim and Pfaff, Ber. 8, 886), 202° (corr.) (P.); and is soluble to the extent of 0·53 vol. in 100 vols. of water. Its aqueous solution is coloured blue by ferric chloride. When fused with caustic potash, it is converted into metahydroxybenzoic acid, and on nitration it yields a trinitro- derivative (m.p. 105°–106°) (Nölting and Salis, Ber. 14, 987; 15, 1858).

Paracresol crystallises in prisms, melts at 36° (Barth, Annalen, 154, 358 [B. and C.]), 36°–37° (T. and S.), and boils at 198° (I.), at 198°–199° (T. and S., B. and C.), at 202° (corr.) (P.); and is soluble to the extent of 1·8 vols. in 100 vols. of water. Its aqueous solution gives a blue colour with ferric chloride. When fused with caustic potash, it is converted into parahydroxybenzoic acid, and on nitration it yields a dinitro- derivative (m.p. 85°) (Richter, Annalen, 230, 313; Nölting and Salis, *l.c.*).

The crude cresol, as obtained from coal tar, is only slightly soluble in water, but its solubility, in an aqueous solution of potassium cresol, renders its employment as an antiseptic possible. This solution is named *solveol* (Lacroix-Hunkiabéyendian, J. Pharm. Chim. 28, 34). The crude cresol is also frequently mixed with soaps, and is used in that form for disinfecting purposes (Dammann, D. R. P. 52129; Frdl. ii. 538; Holmers, D. R. P. 76133 and 80260; Frdl. iv. 1119 and 1120; Raschig, D. R. P. 87275; Frdl. iv. 1121; Engler and Dieckhoff, Arch. Pharm. 230, 561; 232, 351).

Oxidation with peroxides at a high temperature converts the cresols into the corresponding hydroxybenzoic acids (Friedländer and Löw-Beer, D. R. P. 170230; J. Soc. Chem. Ind. 1907, 434).

A mixture of nitro- derivatives, obtained by sulphonating coal-tar cresol and nitrating the sodium salt of the resulting cresolsulphonic acid with nitric acid of sp.gr. 1·2, has been employed, under the names 'Victoria yellow,' 'saffron surrogate' (*q.v.*), as a dye for wool and silk; and, although poisonous (compare Weyl, Ber. 20, 2835; 21, 512), is occasionally used as a colouring matter for butter, cheese, &c. By heating crude cresol with sulphur and alkali sulphide, or with alkalipolysulphides, or with a mixture of sulphur and alkalis, at a high temperature, brown sulphur compounds are obtained which are used for dyeing cotton (Farb. vorm F. Bayer & Co., D. R. P. 102897; Chem. Zentr. 1899, ii. 352).

CRESOLIN. A disinfectant composed of crude phenol and rosin soap.

CRESOLINE YELLOW *v.* AZO- COLOURING MATTERS.

CRESORCINOL *v.* PHENOL AND ITS HOMOLOGUES.

CRESYLIC ACID. The non-crystallisable, higher boiling portion of the phenols obtained in the purification of phenol (*q.v.*) is, after redistillation, known commercially as cresylic acid or liquid carbolic acid. It is a colourless, oily, refractive liquid, does not solidify at −80°, has a sp.gr. 1·044, and consists of 40 p.c. metacresol, 35 p.c. orthocresol, and 25 p.c. paracresol (Schulze, Ber. 1887, 410). It is much less soluble than carbolic acid in water, ammonia, glycerol, or caustic soda, but more readily so in petroleum spirit. It boils at a higher temperature (about 185°–203°), gives a mixture of *m*-tribromo and *o*- and *p*-dibromo derivatives with bromine. It is even more readily acted upon by concentrated sulphuric and nitric acids than carbolic acid (Lunge, Coal Tar and Ammonia, ed. 1900, 182; *v. also* Allen, J. Soc. Chem. Ind. 1890, 141). Its antiseptic properties are more marked than those of carbolic acid or of either of the three cresols.

CRESYL BLUE *v.* OXAZINE COLOURING MATTERS.

CRITH. The weight of a litre of hydrogen at 0° and 760 mm. pressure—viz. 0·0896 gram.

CROCEÏN, BRILLIANT, ORANGE, SCARLETS, *v.* AZO- COLOURING MATTERS.

CROCEÏNE *v.* AZO- COLOURING MATTERS.

CROCIDOLITE. (*Krokydolith*, Ger.) A mineral of the soda-amphibole group, consisting of sodium and iron (ferric and ferrous) silicate, $NaFe'''(SiO_3)_2Fe''SiO_3$. It is known only in a finely fibrous form, its name, in fact, being from *κροκύς, κροκύδος*, wool. In the trade it is known as *blue asbestos*, and it is worked for the same purposes as the other varieties of asbestos (*q.v.*). It is, however, more readily fusible (to a black magnetic glass) than are tremolite-asbestos and serpentine-asbestos. The mineral has been long known from the Asbestos Mountains near the Orange River in Griqualand West, South Africa, where it occurs abundantly as veins, 1 or 2 inches in thickness, in jasper-schists. The closely aggregated parallel fibres are arranged perpendicularly or nearly so to the walls of the veins; and the material is extracted as slabs. Over 100 tons a month are mined for commercial purposes (H. F. Olds, Trans. Inst. Mining and Metall. 1899, vii. 122).

Being an alkali silicate with ferrous iron, crocidolite is especially liable to decomposition when exposed to weathering; sodium is removed, and the iron oxidised and hydrated to form limonite, while the silica is set free. There then results a ferruginous quartz possessing the finely fibrous structure of the original mineral; or, in other words, a pseudomorph of quartz and limonite after crocidolite. This material is coloured a rich golden yellow, and displays a silky lustre, and being at the same time very hard, it is well adapted for ornamental purposes. When cut and polished with a convex surface, it displays a cat's-eye effect, and it is extensively used for making knobs, umbrella handles, beads, &c. Such material is known as *tiger-eye*, though unfortunately in the trade, the name crocidolite is very frequently misapplied to it. The name *pseudo-crocidolite* would be more appropriate. In some stones there has been silicification without oxidation, and the indigo-blue colour of the original crocidolite has been preserved: material of this kind is known as *hawk's-eye*.

L. J. S.

CROCOISITE. Native lead chromate (*v.* CHROMIUM).

CROOKESITE *v.* THALLIUM and SELENIUM.

CROPS. The composition of crops may be regarded from two points of view: (1) the materials they contain, which render them valuable either as food or as sources of some substance of commercial value; (2) the materials they remove from the soil, which must eventually be replaced if the fertility of the land is to be maintained.

In Table I., the composition of some of the principal crops grown in the United Kingdom is set out, cereals being excluded because they are dealt with separately. The composition of each of these materials shows considerable variations, and the analyses given are either typical or the means of a small number of determinations.

TABLE I.—PROXIMATE COMPOSITION OF CROPS.

—	Water	Crude fat	Protein crude	Carbo-hydrates	Crude fibre	Ash
Leguminous:						
Field beans	13·49	1·68	25·31	48·33	8·06	3·13
„ „ haulm	18·40	1·10	8·10	31·00	36·00	5·40
Field peas	13·92	1·89	23·13	52·68	5·68	2·68
„ „ haulm	13·60	1·60	9·00	33·70	35·50	6·60
Clover hay	16·50	2·90	13·50	37·10	24·00	6·00
Lucerne hay	16·50	2·60	14·20	29·20	29·50	8·00
Vetches, green	82·50	0·50	3·20	7·20	5·10	1·50
Root crops:						
Potatoes	74·98	0·15	2·08	21·01	0·69	1·09
Mangolds	87·50	0·14	1·34	8·90	0·98	1·14
Sugar beet	75·00	0·10	1·30	21·40	1·50	0·70
Swede turnips	87·80	0·21	1·54	8·22	1·32	0·91
White turnips	90·78	0·22	1·18	5·89	1·13	0·80
Fosterton hybrid turnips [1]	91·30	—	0·79	6·47	0·94	0·50
Aberdeen yellow [2]	91·09	—	1·14	6·08	1·03	0·66
Carrots	86·79	0·30	1·23	9·17	1·49	1·02
Meadow hay	14·30	2·50	9·70	41·40	26·30	6·20
Seeds hay	14·30	2·70	10·20	36·10	30·20	6·50
Mustard, green	85·10	0·40	2·90	7·30	2·90	1·40

Leguminous crops. The leguminous seeds are distinguished by their high protein content. The proteins of the bean and pea and similar seeds have been studied by Ritthausen (Eiweisskörper der Getreidearten, Bonn, 1872) and Osborne (J. Amer. Chem. Soc. 1898, 20, 410; Amer. J. Physiol. 1908, 23, 180, &c.). The most abundant of these is the so-called legumin (*q.v.*), which, according to Osborne, is a globulin containing lysine. Lentils contain a conglutin which has been hydrolysed, also some edestin.

The leguminous seeds grown in this country contain but a small proportion of oil, which has not received any special examination; the soya bean, however, yields oil up to 20 p.c., and is now being extensively imported from Manchuria and pressed for oil (*v.* SOYA BEAN).

The only carbohydrate in beans, peas, &c., that has received any attention, is the starch, which is abundant and the granules of which possess

[1] Aitken, Trans. H. & Ag. Soc. 1884, 16.
[2] Wilson, *ibid.* 1886, 18.

characteristic shapes. The ash of leguminous plants is distinguished by a large proportion of lime, as may be seen from analyses 5–10 in Table II.

Root crops. In these materials, the ether extract contains little, if any, true fat, the nitrogen-containing substances are also very far from being all protein; usually one-half or more of the nitrogen present is combined in various non-protein forms.

Potatoes.—The characteristic carbohydrate is starch, of which there may be over 20 p.c.; but sugars (both sucrose and reducing sugars) may be present up to 1 p.c., and dextrins or amylans are also present in about the same amount. Amongst the nitrogen compounds there are both insoluble and soluble proteins, part of the latter being coagulable by heat or acids, and a large range of amino- bodies, among which tyrosin has been identified. The non-protein nitrogen may amount to more than half the total nitrogen. The darkening of the juice of a fresh potato is due to the black substance formed by the oxidation of the tyrosine under the action of an enzyme, also present in the cells. The darkening of boiled potatoes is due to some other cause (Ashby, J. Agric. Sci. 1905, i. 348). About two-thirds of the ash of potatoes consist of phosphoric acid and potash.

Mangolds.—The characteristic carbohydrate present in the mangold is sucrose, which constitutes about 8 p.c. of the weight of the root, the total dry matter amounting to about 13 p.c. About 0·25 p.c. of reducing sugar is also present. The variation in the sugar content of mangolds has been examined by Wood (J. Agric. Sci. 1905, 1, 176), who gives the following table:—

Variety	Yield per acre—tons	Dry matter p.c.	Sugar p.c.	Nitrogen p.c.
White-fleshed globe .	29·9	10·7	6·3	0·165
,, ,, intermediate	27·4	12·0	7·1	0·168
Yellow-fleshed tankard .	24·6	13·1	8·0	0·186
,, ,, globe .	25·0	13·4	8·2	0·191
Long red . . .	29·9	13·1	7·9	0·157

Of the nitrogen in mangolds, only 30–50 p.c. is in the protein form, 20–40 p.c. is combined as amide or amino- acid and is liberated on hydrolysis as ammonia, while 10 p.c. may be in the nitric form.

On storage, the mangold loses sugar by respiration. and some of the sucrose becomes changed into reducing sugar, a process which is much accelerated as soon as the temperature rises in the spring (*see* Miller, J. Roy. Agric. Soc. 1900, 61; 1902, 63).

Sugar beet.—In the sugar beet, which has been derived from the same species of *Beta* as the mangold, the characteristic carbohydrate is likewise sucrose, which may be present to the extent of 20 p.c. It is always accompanied by a certain proportion of reducing sugars (glucose and maltose), which, in well-grown roots, should not exceed 1 p.c. of the sucrose.

The variations in the amount and nature of the sugars in sugar beet have been subjected to very detailed investigation, for accounts of which the numerous technical works dealing with the beet-sugar industry, such as Briem, Der Praktische Rübenbau, should be consulted.

The nitrogenous constituents resemble those of the mangold (*see* Lippmann, Ber. 1896, 29, 2645).

Swedes and turnips.—In these closely allied roots, the carbohydrates consist of sugars (chiefly reducing sugars, though few data exist) and pectic bodies yielding a mucilage on boiling with water. In Wilson's analyses, already quoted, the sugars averaged 4·72 p.c. The nitrogen compounds are also largely non-protein, only from 30 to 50 p.c. consists of protein. It is generally considered that swedes and turnips grown in the north and especially in the east of Scotland, possess a higher feeding value than the roots grown in the south; analytical data to confirm this opinion are, however, lacking, though it is certain that much larger crops are usually grown in the cooler climate of the north, where the crop can be sown earlier with success.

Ash of crops. In Table II. are collected various analyses of the ash of the crops above mentioned.

TABLE II.—COMPOSITION OF THE ASH OF FARM CROPS.

——	Ash in dry matter	N in dry matter	Fe_2O_3	CaO	MgO	K_2O	Na_2O	P_2O_5	SO_3	Cl	CO_2	SiO_2
1. Potatoes .	3·99	0·88	0·35	1·53	3·48	58·27	0·06	12·86	5·87	7·27	11·37	0·58
2. Mangolds .	6·70	1·31	0·44	3·58	2·13	35·90	19·34	9·34	3·25	3·87	21·43	0·97
3. Swedes .	5·58	2·31	0·61	12·12	3·02	39·17	5·24	9·83	13·49	2·48	12·43	0·72
4. Grass .	7·21	1·65	0·49	12·43	3·83	29·76	4·09	7·04	6·17	8·78	10·31	18·32
5. Clover .	8·15	2·92	1·03	37·37	5·10	13·10	0·58	3·75	1·82	2·26	34·96	0·54
6. Beans, corn	3·27	4·32	0·48	5·60	6·61	40·58	2·12	30·69	6·35	2·43	5·28	0·41
7. ,, straw	5·80	0·94	1·54	28·39	3·12	8·07	14·57	2·31	3·30	2·49	33·68	3·08
8. Peas, corn	2·53	3·87	0·07	5·74	8·97	44·31	0·39	29·30	10·42	0·45	—	0·37
9. ,, straw	5·87	—	1·03	40·34	8·30	11·78	9·90	8·26	6·76	3·84	—	10·66
10. Lucerne .	8·71	—	2·68	24·74	6·27	41·91	1·22	7·71	5·63	8·05	—	3·16
11. Flax, seed	3·82	—	1·54	10·96	11·47	27·85	4·15	41·27	2·01	0·63	—	1·47
12. ,, stem	3·70	—	6·62	25·16	4·99	25·56	10·16	8·94	4·02	6·64	—	9·40
13. Hops, cones	11·25	—	1·80	16·77	5·66	28·35	1·99	13·73	5·01	4·35	—	22·32
14. ,, leaves	18·00	—	0·64	40·17	5·32	13·65	3·79	7·82	3·49	4·02	—	22·21
15. ,, stems	4·70	—	1·07	29·59	8·34	26·18	5·06	11·23	3·41	8·87	—	8·29
16. Tobacco .	16·27	—	2·93	42·34	11·22	17·48	4·26	3·22	4·28	4·87	—	10·11

Analyses 8–16 are means taken from Wolff's Aschen-analysen, and have been recalculated to exclude the carbon dioxide present in the ash, as obtained after burning. Analyses 1–7 are selected from the Rothamsted records.

Materials removed from the land by average crops. Table III., compiled by Warington from Rothamsted data, shows the amount of the three important constituents—nitrogen, phosphoric acid, and potash, which would be contained in an average crop of the magnitude indicated, and therefore have been removed from the soil by the crop, except in the case of the nitrogen contained in leguminous crops.

TABLE III.—AMOUNT OF FERTILISING CONSTITUENTS PER ACRE REMOVED BY AN AVERAGE CROP.

—	Weight of crop, dry	Nitrogen	Potash	Phosphoric acid
	lbs.	lbs.	lbs.	lbs.
Wheat, 30 bushels, straw 28 cwts. . . .	4183	50	28·8	21·1
Barley, 40 „ „ 22 „ . . .	3827	49	35·7	20·7
Oats, 45 „ „ 25 „ . . .	3978	52	46·1	19·4
Maize, 30 „ „ 19 „ . . .	3377	43	36·3	18·0
Meadow hay, 1½ tons	2822	49	50·9	12·3
Red clover hay, 2 tons	3763	98 [1]	83·4	24·9
Beans, 30 bushels, straw 20 cwts. . . .	3461	107 [1]	67·1	29·1
Turnips, 17 tons, leaf 5 tons . . .	4657	110	148·8	33·1
Swedes, 14 „ „ 2 „	4055	98	79·7	21·7
Mangolds, 22 „ „ 8 „	7568	149	300·7	52·9
Potatoes, 6 „ tubers	3360	46	76·5	21·5

A comparison of these figures with the amount of fertilising material usually provided for the crops in question, or the effects of particular manures in field experiments, serves to show that the data contained in Table III. afford no guidance in deciding the appropriate manure for each crop.

The earliest theory of plant manuring, that of Liebig, supposed that the requirements of the plant can best be satisfied by applying to the land exactly the constituents taken away by a good crop of that particular kind; but the results of the Rothamsted experiments, confirmed by general farming experience, very soon showed that this view was incorrect, because it failed to take into account the enormous amount of plant food contained in the soil, more or less of which would reach the plant according to the method of cultivation and the plant's habit of growth. Moreover, in practical farming the supply of manure is largely determined by the place the crop occupies in the rotation and the treatment which has been given to the previous crops. To take an example, wheat and barley withdraw almost the same fertilising materials from the soil, yet all farming experience goes to show that the yield of wheat is chiefly determined by the supply of nitrogen. If this element is present in sufficient quantity the wheat plant with its long period of growth is usually able to satisfy its requirements for phosphoric acid and potash from the soil. With barley, nitrogen is still a most important element in nutrition, but phosphoric acid also exerts a striking beneficial action and is a necessary element in the fertiliser. Neither for wheat nor barley need potash be supplied except on very light soils. A still more noteworthy example is provided by the swede turnip crop. The table shows that an average crop will take away from the soil about 100 lbs of nitrogen, 20 lbs. of phosphoric acid and 80 lbs. of potash, yet the usual fertilisers applied to swedes consist almost wholly of phosphatic compounds, with a comparatively small amount of nitrogen and no potash. The majority of the swedes grown in this country receive from 50 to 100 lbs. of phosphoric acid (*i.e.* about 5 cwt. of superphosphate or basic slag), and the small quantity of nitrogen that would be provided by a light dressing of farmyard manure or half a hundredweight of sulphate of ammonia. The fertilising requirements of a crop are in fact conditioned by the soil (*q.v.*) rather than by its composition.

A. D. H.

[1] Wholly or in part derived from the atmosphere.

CROTON OIL is obtained from the seeds of *Croton Tiglium* (Linn.), a tree belonging to the *Euphorbiaceæ*, indigenous to the Malabar coast, and cultivated in Southern Asia and China. The seeds contain 53–56 p.c. of oil.

The oil has an amber-yellow, orange, or brown colour, according to its age; it has a nauseous odour, a burning taste, and acts as a very powerful purgative.

The chemical composition of croton oil differs so widely from that of all other oils, that its recognition, by means of the 'quantitative reactions' (*see* OILS AND FATS), is easy. It contains a considerable amount of volatile acids; hence its Reichert-Meissl value is about 13; its iodine value is 103–104. Croton oil is strongly dextro-rotatory.

J. L.

CROWN GLASS *v.* GLASS.

CRUCIBLES. A perfect crucible should withstand the highest temperatures without fusion, should bear sudden changes of temperature without fracture, and should be unacted upon by the materials which are to be heated in it. A semi-automatic apparatus for moulding crucibles has been patented by Sims (Eng. Pat. 445, 1888).

Clay crucibles are prepared from selected clay; of the Stourbridge clay worked, only about 5 p.c. is available for this purpose. Its plasticity is much increased by exposure for some months in a moist condition to the air. During this process of 'weathering' it becomes disintegrated, and the removal of foreign matter is thereby facilitated. The presence of iron pyrites is especially injurious; furnace gases convert it into the oxide which acts as a flux and forms cavities

in the crucible. Lime is also hurtful, except when in very small quantities and uniformly distributed. Potash and soda are invariably present in clay, and when in small quantity increase the coherence of the crucible without appreciably impairing its power of withstanding the action of heat.

In order to reduce the tendency to crack, and to increase its refractory character, the clay is usually mixed with sand, ground flints, burnt clay (old broken crucibles), graphite or coke. These, which are either less fusible than the clay or altogether infusible, form a skeleton which upholds and prevents deformation of the crucibles at temperatures at which the clay would tend to fuse. The most refractory crucibles contain the largest proportion of silica.

The clay, which should be of the greatest possible fineness, is well beaten to remove air bubbles and mixed with the proper quantity of the refractory material. According to Berthier (Traité des Essais, 1, 66), when silica is used, it should not be too fine, as the tendency to combine with the clay and thus increase the fusibility would thereby be increased. Crucibles of fine grain are also more liable to fracture.

Small crucibles are usually baked in a kiln, but the large casting pots of Stourbridge clay are not baked until immediately before use. When the temperature of the baking is high, the crucible is more liable to fracture on reheating.

All clay crucibles are more or less acted upon by litharge, but metals and most ores may be heated in them without danger. Berthier recommends a lining of such material as silica, alumina, or magnesia previously moistened. A lining of chalk renders a crucible less permeable to litharge.

Queneau recommends lining clay crucibles, before drying, with some substance which will resist the chemical reactions for which they are designed and then compressing strongly, drying, and firing (Fr. Pat. 354319; J. Soc. Chem. Ind. 1905, 1071).

Crucibles may be rendered non-porous by treating with ferrous sulphate solution and firing (Mitchell, U.S. Pat. 894845; J. Soc. Chem. Ind. 1908, 886) or by the addition to the clay of chromic oxide, chromites or chrome iron ore, which also renders them much more refractory (Bach, Eng. Pat. 24041, 1903; Klein, U.S. Pat. 787770; Seigle, Fr. Pat. 383593; and Placet, Eng. Pat. 28728, 1896).

The fracture of crucibles by expansion of solidifying metal can be prevented by lining with friable material (Colby, U.S. Pat. 830208; J. Soc. Chem. Ind. 1906, 934).

Goldschmidt recommends that crucibles for the 'Thermit' process should be lined with a mixture of magnesia or carborundum and soluble glass (Fr. Pat. 354597; J. Soc. Chem. Ind. 1905, 1114).

Very large crucibles may be built up from cylinders or annular rings of refractory material, provided arrangements are made for tapping the contents without moving the crucible (Reynolds, Eng. Pat. 1004, 1901; Rousseau, Eng. Pat. 7451, 1902).

Stourbridge clay crucibles are made from a mixture of raw ground clay with about one-half its weight of powdered, sifted, old glass pots, from which all adherent glass has been removed, the mixture being made in a disc mill, and kneaded to the proper consistency. Percy gives the composition of the Stourbridge clay used for the best crucibles as silica, 79·25; alumina, 13·57; iron oxide, 1·38; lime, 0·08; magnesia, 0·42; water, 5·11.

The following analyses show the composition of certain varieties of crucibles. Nos. 1–7 are by Berthier, No. 8 by Dick, Nos. 9–12 by Brand, and Nos. 13–15 by Mène :—

—	Silica	Alumina	Iron oxide	Magnesia	Lime	Potash	Sulphur	Carbon	Water
1. French, made by Beaufay at Paris	64·6	34·4	1·0	—	—	—	—	—	—
2. French, made by Deyeux at Savignies	72·3	19·5	3·9	—	—	—	—	—	1·8
3. Hessian	70·9	24·8	3·8	trace	—	—	—	—	—
4. English steel	71·0	23·0	4·0	—	—	—	—	—	—
5. St. Etienne steel	65·2	25·0	7·2	trace	—	—	—	—	—
6. Glass pots, Nemours	67·4	32·0	0·8	trace	—	—	—	—	—
7. „ „ Bohemia	68·0	29·0	2·2	0·50	—	—	—	—	—
8. Cornish, made by Juleff	72·39	25·32	1·07	trace	0·38	1·14	—	—	—
9. Steel crucible; clay	53·92	40·57	—	—	—	—	0·230	—	—
10. „ „ coke clay	42·78	34·71	—	—	—	—	0·490	18·60	—
11. „ „ graphite	24·63	27·89	—	—	—	—	0·270	40·43	—
12. Magnesia	4·80	2·49	—	92·62	—	—	0·099	—	
13. English blacklead	51·4	22·0	3·5	—	0·2	—	—	20·0	1·8
14. Ditto	45·1	16·65	0·95	—	—	—	—	34·5	2·5
15. Ditto	50·0	20·0	1·5	—	0·5	—	—	25·5	3 0

Hessian crucibles are composed of equal weights of Almerode clay and sand. They are usually triangular, of coarse texture, porous, rapidly destroyed by litharge, and liable to fracture on sudden change of temperature, but will withstand a very high degree of heat.

French crucibles are made from a mixture of 1 part raw Ardennes clay and 2 parts of the same which has been burnt. They are refractory and of fine texture.

Cornish crucibles are largely used for copper assaying. They are round, of coarse grain, and of a mottled greyish-white colour. They are kiln-burnt, and withstand sudden changes of

temperature, but cannot be heated to whiteness. Cornish crucibles are now made by the Morgan Crucible Company at Battersea.

London crucibles are of reddish-brown colour and close texture. They will not stand sudden change of temperature, but withstand the action of litharge fairly well.

Silica crucibles may be made of powdered silica, mixed with a highly absorbent substance, *e.g.* kieselguhr, saturated with water (Sankey, Eng. Pat. 3353, 1906; J. Soc. Chem. Ind. 1907, 96). Sand, mixed with a small proportion of cement and water, moulded, dried, and heated to the fusing-point of the sand, forms a very refractory material (Reppey, U.S. Pat. 905295; J. Soc. Chem. Ind. 1909, 24). A mixture of sand with a little lime may be used (Berglund, Fr. Pat. 366830; J. Soc. Chem. Ind. 1906, 1081).

White fluxing pots are made by the Morgan Company from a highly refractory fireclay from Rouen. Crucibles containing carbon are now largely used. For very high temperatures, crucibles cut from a block of gas carbon or similar material may be employed. Clay crucibles may also be filled with a moist mixture of charcoal with starch, treacle, gum-water, or oil, or, for large crucibles, gas tar. The mass is forced with considerable pressure into the crucible and is then cut out, leaving a coating of about $\frac{1}{8}$ inch in thickness, or the coating is put into the crucible and smoothed with a glass rod. The crucible is then filled with powdered charcoal and heated to redness.

Graphite crucibles. For the fusion of metals, plumbago or coke crucibles are of great value, but they are not largely used for assaying. At the Battersea works, the following process of manufacture is employed: hand-picked Ceylon plumbago is ground, sifted, digested with dilute sulphuric acid to remove the greater part of the iron, and mixed and kneaded to a stiff paste, with about an equal weight of fine fireclay. The mixture is passed through a pug-mill, and is cut into blocks. When required for use, the blocks are again passed through the mill, and made by hand on a wheel or moulded by machinery. They are then dried and baked in saggars. These crucibles may be protected from oxidation by lining them with clay (Woolford, Eng. Pat. 24479, 1898; J. Soc. Chem. Ind. 1900, 52; McDonald, U.S. Pat. 828954; J. Soc. Chem. Ind. 1906, 911).

They are of fine grain, and will withstand the highest temperatures and repeated sudden changes. The graphite is slowly oxidised by metallic oxides or by the furnace gases. To minimise this, the crucible may be coated by dipping in a paste of clay and solution of borax. Any iron which is present in the graphite is liable to become introduced into the melt, and the carbon itself combines with iron or steel (*v.* Brand, Chem. Zentr. 15, 407; and Dingl. poly. J. 256, 227).

Tar, rosin, &c., may be used to bind the clay and graphite in manufacturing these crucibles (Putz, D. R. P. 181979; J. Soc. Chem. Ind. 1907, 1030). Digby recommends (Eng. Pat. 3661, 1893) the following composition:—

Plumbago, 17-mesh granules	.	17	parts
Plumbago, 80- ,, ,,	.	2	,,
Russian clay	.	5	,,
China-stone	.	5	,,
Gas carbon	.	2	,,

The last three ingredients are ground and mixed with water and then the plumbago is added and the crucibles formed, dried at 65° and baked.

Salamander crucibles, made by the Morgan Company, contain a much smaller proportion of carbon. They withstand sudden changes of temperature perfectly.

Lime crucibles are cut from blocks of well-burnt (preferably slightly hydraulic) lime.

Magnesia was introduced by Caron as a refractory basic material for making crucibles or for lining reverberatory furnaces for melting and dephosphorising steel. Magnesia contracts considerably when heated; it is therefore necessary, before making it into bricks or crucibles, to expose it to a higher temperature than that to which it will be heated. The strongly calcined magnesia is made into a paste with 15–30 p.c. of raw (slightly calcined) magnesia, and 10–15 p.c. of water, and is moulded, dried, and baked at a red heat. The highly heated magnesia would not cohere without admixture with the raw material. Magnesia crucibles are not injured by exposure to the atmosphere. Gaudin makes crucibles from a mixture of 1 part magnesia and 1 part bauxite. They may also be formed from a mixture of calcined magnesite with from 2 p.c. to 12 p.c. of a boron compound (according to the amount of calcium present), moistened, moulded, dried and fired at a high temperature (Rawson and Littlefield, Eng. Pat. 16004, 1900; J. Soc. Chem. Ind. 1901, 992, and *ibid.* 1902, 52). The product is said to resist molten litharge. Porous crucibles for metal refining, are made from a similar mixture with the addition of sawdust (Dobell, Eng. Pat. 10715, 1897).

Alumina crucibles withstand sudden changes of temperature, and are not affected by the materials fused, even sodium being without action. According to Deville's process (Ann. Chim. Phys. [3] 46, 195), alumina precipitated at low temperature from ammonia alum solution is mixed with an equal weight of powdered marble, and is exposed to the highest temperature of a wind furnace. The mixture so produced, which may be considered as consisting of calcium aluminate, is mixed with its own weight of moist, precipitated alumina, and is made into a crucible, dried and baked (*see also* Caspar, U.S. Pat. 886111; J. Soc. Chem. Ind. 1908, 568). When the crucible is required to withstand higher temperatures, the amount of the calcium aluminate may be reduced, but the proportion of lime should not fall below 10 to 20 p.c.

Bauxite has been used to replace alumina. It is extremely refractory (*v. Bauxite,* art. ALUMINIUM).

Carborundum crucibles are infusible and resistant to chemical action and have great solidity. They may be made from a mixture of commercial carborundum with sufficient clay to render it plastic (Velter, Fr. Pat. 376179; J. Soc. Chem. Ind. 1907, 1010; Engels, Eng. Pat. 14567, 1901).

A mixture of powdered silica rock or ganister with carborundum or amorphous silicon carbide, may be used. It is mixed with water-glass solution or glue, &c., compressed to shape and heated to the temperature of the electric furnace

(Imray and Carborundum Co. Eng. Pat. 19493, 1902; 3308, 1903) (*see also* CARBORUNDUM).

(*See* further, Kerl, Handb. Thonvaaren Ind. 1879, 528–534; and Percy, Metallurgy (Fuel, &c.), 1875, 110–141.)

CRUMPSALL YELLOW *v.* AZO- COLOURING MATTERS.

CRURIN. Trade name for quinoline bismuth thiocyanate, used as an antigonorrhoic.

CRYOLITE. (*Kryolith*, Ger.) A native fluoride of aluminium and sodium, found almost exclusively in Greenland, whence it has been sometimes called 'Greenland spar.' The name cryolite, or 'ice-spar' (*Eisstein*) refers to the general resemblance of the mineral to ice (*κρύος*) and to its ready fusibility in a candle flame. The mineral was discovered by the Danes in 1794, and described in the following year by Schumacher. Nearly all the cryolite of commerce is obtained from a single locality at Ivigtut (or Evigtok), on Arsuk-fjord in south Greenland. This locality was visited by Giesecké, and later by J. W. Tayler (Quart. Jour. Geol. Soc. 12, 140). The cryolite occurs as a large deposit in gneiss, and contains (especially near its junction with the enclosing rock) a number of metallic minerals, such as galena, pyrites, and chalybite (*v.* P. Johnstrup, N. Jahrb. f. Min. 1886, I, Ref. 28; R. Baldauf, Zts. prakt. Geol. 1910, xviii. 432).

Cryolite is usually found in cleavable translucent masses, of snow-white colour, with a vitreous lustre. H. 2·5; sp.gr. 2·9–3. Crystals are rare, and their relations have been the subject of much discussion; they are cube-like in habit, and belong to the monoclinic system. Although cryolite is usually white, it is sometimes coloured brown or reddish, and is said to pass downwards, in the Greenland deposit, into a black mass. The black variety loses its colour when heated. Before the blowpipe cryolite fuses to a white enamel.

The composition of cryolite may be represented by the formula $3NaF{\cdot}AlF_3$. This corresponds to 12·8 p.c. Al, 32·8 Na, and 54·4 F. An analysis of the Greenland cryolite by Chodnew yielded 13·23 p.c. Al, and 32·71 Na, with 0·83 of Mn_2O_3 and MgO (Verh. Petersb. Min. Ges. 1845–6, 209). Durnew found in the cryolite of Miask in the Urals, 13·41 p.c. Al, 32·31 Na, 0·55 Fe_2O_3 and Mn_2O_3, and 0·35 CaO (Pogg. Ann. 83, 587). Deville found in the Greenland cryolite 0·018 p.c. of vanadic acid and a small proportion of phosphoric acid. An analysis of cryolite from near Pike's Peak, Colorado, by Cross and Hillebrand yielded Al 12·9, Na 32·4, F 53·55, Fe_2O_3 0·4, Ca 0·28, H_2O 0·3 (Amer. J. Sci. [3] 26, 1883, 271).

Cryolite was formerly a rare mineral, but about 1855 it was introduced into Europe commercially, and at once found numerous applications in the arts. About 10,000 tons are now exported annually from Greenland. By heating finely powdered cryolite with sodium or with magnesium, J. Percy and A. Dick obtained metallic aluminium (Phil. Mag. 10, 1855, 364). Deville found that fused cryolite is decomposed by the passage of an electric current, with elimination of free aluminium. At the present time, aluminium is prepared by the electrolysis of bauxite, but the addition of some cryolite is necessary to start the process and to keep it in continuous operation.

A wide range of applications was suggested when Julius Thomsen showed in 1850 that cryolite is readily decomposed by heating with calcium carbonate, and that sodium aluminate may be thus obtained:

$$Al_2F_6{\cdot}6NaF+6CaCO_3 = 3Na_2O{\cdot}Al_2O_3+6CaF_2+6CO_2.$$

If heated with quicklime, a similar decomposition is effected, of course without evolution of CO_2. The sodium aluminate has been used in the manufacture of alum, and in the preparation of caustic soda for soap making. By lixiviation, the aluminate is easily dissolved out; and by the passage of CO_2 through the solution, Na_2CO_3 is obtained, while alumina separates in a gelatinous form. The decomposition of cryolite may also be effected by boiling the finely pulverised mineral with milk of lime. By adding an excess of powdered cryolite to the resulting solution, the aluminate is decomposed, the alumina being precipitated, while sodium fluoride remains in solution:

$$3Na_2O{\cdot}Al_2O_3+Al_2F_6{\cdot}6NaF=2Al_2O_3+12NaF.$$

Cryolite can be readily decomposed by the action of sulphuric acid, with formation of sodium sulphate, which can be easily converted into carbonate; but the process, after trial at Copenhagen, has been abandoned in consequence of the inconvenience arising from the evolution of hydrofluoric acid:

$$Al_2F_6{\cdot}6NaF+6H_2SO_4 = Al_2(SO_4)_3+3Na_2SO_4+12HF.$$

The manufacture of soda from cryolite is carried on at Oersund in Denmark, and at Natrona, near Pittsburg in Pennsylvania. The mineral is also employed in the preparation of an opaline glass, somewhat resembling porcelain. This glass may be formed by fusing together 100 parts of silica, 35 or 36 of cryolite, and 13 or 14 of oxide of zinc. C. Weinreb has investigated the cause of the milkiness of cryolite glass, and believes that it is due to the presence of aluminium fluoride, which on the cooling of the fused mass, separates in a highly comminuted condition, and being distributed through the glass renders it more or less opaque (Dingl. poly. J. 256, 361). L. J. S.

CRYOSCOPY. So long ago as 1788 Blagden proved that the extent to which the freezing point of an aqueous solution lies below that of water—the depression of the freezing point, as it is called—is proportional to the concentration of the dissolved substance. Nearly a century later, the researches of de Coppet and Raoult showed that when equimolecular proportions of different substances are dissolved in equal quantities of a given solvent, the solutions so obtained have, in general, the same freezing point. It is on these facts that the use of the cryoscopic method of determining the molecular weights of dissolved substances is based.

In comparing the effects of different sub stances on the freezing point of a given solvent, it is obviously convenient, in view of de Coppet's and Raoult's results, to refer these effects to 1 gram molecule of solute and to some definite quantity of the solvent: in practice, 100 grams of the latter are taken as the standard amount. The depression of the freezing point for such a

concentrated solution as one containing 1 gram molecule of solute in 100 grams of solvent cannot be determined directly: it is calculated from the depression observed for a dilute solution, on the basis of the proportionality between depression and concentration. An example may be taken to illustrate this point. A solution containing 0·609 gram of ethyl alcohol in 100 grams of water freezes 0·243° below the freezing point of water; from these data it follows, if proportionality between depression and concentration is assumed, that the depression for a solution containing 1 gram molecule of alcohol in 100 grams of water would be $\frac{0·243×46}{0·609} = 18·4°$. Again, a solution of 4·276 grams of sucrose in 100 grams of water, freezes 0·237° below the freezing point of water; from these data it follows, as above, that the depression for a solution containing 1 gram molecule of sucrose in 100 grams of water would be $\frac{0·237×342}{4·276} = 19·0°$. If the depressions produced by 1 gram molecule of other non-electrolytes in 100 grams of water are similarly calculated from experimental data, values are obtained which are very close to the figures already quoted. The depression, therefore, for a solution containing 1 gram molecule of non-electrolyte in 100 grams of water is a constant, independent of the particular solute; the average value of the constant for water, deduced in the empirical way just described, is 18·5°.

For each solvent, a characteristic constant (k) can be similarly deduced from experimental data. The evaluation of this constant—the 'molecular depression of the freezing point'—is effected, as illustrated above, by the formula $k = \frac{M}{g} \cdot \Delta t$, where Δt is the depression of freezing point observed for a solution containing g grams of solute in 100 grams of solvent, and M is the molecular weight of the solute.

It has been shown by van't Hoff that, on thermodynamical grounds, the molecular depression of the freezing point for any solvent is quantitatively related to the temperature of freezing and to the latent heat of fusion. The relationship in question is $k = \frac{0·0198T^2}{\omega}$, where T is the freezing point of the solvent on the absolute scale, and ω is the latent heat of fusion per gram of the solvent. The following table shows how far the values of the molecular depression, calculated for various solvents by van't Hoff's formula, are in agreement with those deduced empirically:—

Solvent	k Empirical	k Calculated
Water	18·5°	18·6°
Formic acid	28°	27·5°
Acetic acid	39°	38·5°
Benzene	50°	52°
Naphthalene	68·5°	69°
p-Toluidine	53°	51°
Phenol	75°	74°

The formula $k = \frac{0·0198T^2}{\omega}$ is based on the assumption that, when a solution freezes, it is the pure solid solvent which crystallises out. It is not surprising, therefore, that in cases where the crystals separating from the solution contain some of the dissolved substance, *e.g.* solutions of thiophene in benzene, the empirical value for the molecular depression, deduced in the usual way, differs considerably from the normal value. In such cases the depression observed is smaller than it would be if the pure solid solvent separated out.

When the value of k for any solvent has been ascertained, either empirically by experiments with normal substances of known molecular weight, or indirectly by van't Hoff's formula, it may be utilised in determining the molecular weights of new substances. For this purpose, the formula $k = \frac{M}{g}\Delta t$ is employed, but now k is taken as known, and M is the quantity to be evaluated: in view of this, the equation may be written $M = \frac{k.g}{\Delta t}$.

It is evident that a determination of the molecular weight of a dissolved substance by the cryoscopic method depends, not on the absolute freezing temperature of the solution, but on the difference between the freezing point of the solvent and that of the solution. This difference can be determined with greater accuracy than can the freezing temperatures themselves. A thermometer with a very open scale, covering only 5°–6°, is employed, and it is convenient, as suggested by Beckmann, to have a reservoir attached to the upper end of the thermometer tube, so that the quantity of mercury in the bulb and stem may be varied according to requirements. This device permits the use of one and the same thermometer at different temperatures, and therefore with various solvents. In Beckmann's thermometer, which is the one usually employed in cryoscopic investigations, the scale degree is about 4 cm. in length and is divided in hundredths: with the aid of a lens, preferably adapted for sliding up and down the stem, it is possible to estimate 0·001°. The form of the reservoir attached to the upper end of the ordinary Beckmann thermometer is shown in the accompanying sketch. When it is desired to adjust the thermometer for experiments with any given solvent, the bulb is immersed in water of the same temperature as the freezing point of the solvent. If the top of the mercury thread should reach a steady position on the upper half of the scale, no further adjustment is needed. Should the mercury, after sufficient time has been allowed, extend beyond the scale and into the reservoir, it is necessary to detach a portion. This is effected by putting the bulb in water 2°–3° higher than the required temperature, and then gently tapping the upper end of the thermometer until the mercury hanging at the top of the reservoir is separated from the thread. On cooling down again to the freezing temperature of the solvent, the top of the thread should now come to rest somewhere on the upper half of the scale. If the quantity of mercury in the bulb and stem is too small, so that when the thermometer is immersed in

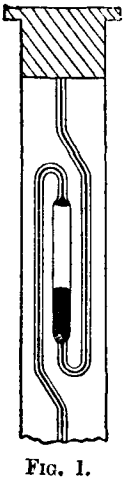


FIG. 1.

water of the same temperature as the freezing point of the solvent, the thread does not reach the scale or appears only on the lowest part of it, the bulb is warmed until the mercury appears at the top of the reservoir. By a throwing movement, some of the mercury at the bottom of the reservoir is jerked up to the top, where it joins the end of the thread. The bulb is then immersed in water 2°–3° above the temperature required, and the final adjustment is carried out in the way already described.

The cryoscopic apparatus commonly employed for the determination of the molecular weight of dissolved substances is that known as Beckmann's. The accuracy of this method, as ordinarily applied, is not great, the error being of the order ±5 p.c. For most laboratory purposes, however, this is sufficient, and it is only when extreme accuracy is required, as in the investigation of very dilute aqueous solutions, that special forms of apparatus have to be employed.

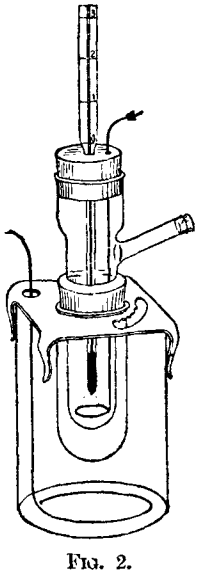


FIG. 2.

The essential parts of Beckmann's apparatus are seen in the subjoined diagram. A stout glass jar, holding about 1½ litres, is provided with a metal top, at the side of which is a hole for a stirrer, and in the middle of which is another hole capable of holding a large stout test-tube, 3–4 cm. in diameter. The lid and the tube are held in position by springs, as will be evident from the diagram. By means of a cork, there is fitted in the tube another, narrower one, to hold the liquid under investigation. This tube should preferably have a flat bottom, while the part of it which projects beyond the outer jacket is provided with an auxiliary side tube, and is itself widened out at the upper extremity. The cork with which this inner tube—the freezing tube, as it may be called—is fitted carries the thermometer, and allows also free passage to a stirrer. The latter is best made of stout platinum wire, but silver or nickel may be used, provided that the possibility of chemical action is excluded. The thermometer must be fitted in an accurately central position, so that the stirrer may be moved up and down without grating.

When a determination of molecular weight is to be made, the freezing tube is charged with a weighed quantity of the solvent, usually 10–20 grams, and the jar is filled with water or a mixture of ice and salt kept at a temperature 4°–5° below the freezing point of the solvent under examination. The freezing tube, with thermometer and stirrer, is immersed directly in the jar, until the temperature has fallen almost to the freezing point. It is then set in the jacket tube and the contents are stirred regularly, while the mercury in the thermometer falls slowly. The fall continues until the solvent is more or less supercooled. In the majority of cases, freezing sets in spontaneously before the supercooling exceeds 0·5°, and the liberation of heat results in a rise of the mercury in the thermometer up to a steady maximum position. This is the freezing point of the solvent—the temperature at which liquid and solid solvent are in equilibrium with each other. It is advisable, when the thread is rising towards its steady position, to tap the thermometer before taking a reading, and so avoid the possibility of the mercury sticking in the capillary. Should the supercooling exceed 0·5°, crystallisation ought to be initiated, either by stirring very vigorously for a few moments or by introducing a tiny crystal of the solid solvent. Whenever freezing has begun, the solvent must then be stirred with uniform regularity until the constant temperature has been reached.

The freezing point of the solvent having been determined two or three times in the manner just described, a weighed quantity of the solute, enough to give a depression of not less than 0·2°, is introduced, and the freezing point of the solution is then ascertained in the same way as that of the solvent. Subsequent additions of solute are made and the resulting depressions determined as before. One addition, it is true, yields sufficient data for the calculation of the molecular weight of the solute, but it is desirable to ascertain also whether the concentration of the solute has any definite and notable influence on the value obtained for its molecular weight. It is advisable, further, to redetermine the freezing point of the solvent at the end of such a series of experiments, and so obtain a guarantee that the zero of the thermometer has not changed appreciably during the course of the work.

Various suggestions have been made from time to time with the object of rendering the simple Beckmann apparatus a more accurate instrument. Thus it has been proposed to stir the contents of the freezing tube mechanically instead of by hand. The access of atmospheric moisture to a hygroscopic solvent may be prevented by passing a current of dry air into the freezing tube during an experiment, or by using as stirrer an iron ring which is enveloped in platinum foil and is operated electromagnetically. In this latter case, obviously, communication between the contents of the freezing tube and the outside air can be completely cut off. The same end is attained by employing an ordinary stirrer with a mercury valve. (For a detailed description of these modifications and additions, *see* Beckmann, Zeitsch. physikal. Chem. 1891, 7, 323; 1896, 21, 239; 1897, 22, 616; 1903, 44, 169; *also* Ostwald and Luther's Physiko-chemische Messungen.)

For the determination of the freezing point of liquids which are obtainable only in small quantities—physiological fluids, for example—Beckmann's apparatus, in its ordinary form, is too large. Modifications of this apparatus, suitable for the investigation of blood, urine, &c., have been suggested by various authors (Guye and Bogdan, J. Chim. Phys. 1903, 1, 379; Burian and Drucker, Zentr. Physiol. 1910, 23, 772). In these instruments, only 1–2 cub.cm.

of liquid is required, and it is claimed that the accuracy is of the same order as that attainable with the ordinary Beckmann apparatus. In this connection, mention ought to be made also of Eykman's apparatus (Zeitsch. physikal. Chem. 1888, 2, 964; 1889, 4, 497). This consists of a small flask, holding about 10 cub. cm., into the neck of which is ground a thermometer, graduated in tenths or hundredths of a degree. There is no separate jacketing vessel, but the procedure is similar to that followed in the case of the Beckmann apparatus.

As regards the preparation of the cooling bath required in the cryoscopic investigation of aqueous solutions, the usual mixture of ice and common salt solution may be replaced in some cases by a mixture of ice and a solid salt, which gives a steady eutectic temperature. Salts suitable for this purpose, with the eutectic temperatures obtained when they are mixed with ice, are alum, −0·47°; sodium sulphate, −0·7°; potassium dichromate, −1·0°; potassium sulphate, −1·5°; copper sulphate, −2·0°; potassium nitrate, −3·0°; zinc sulphate, −5·0°; barium chloride, −7·0°. Another kind of cooling bath was used by Raoult, who surrounded the jacketed freezing tube with ether, and passed through the latter a current of dry air (Compt. rend. 1896, 123, 476; Zeitsch. physikal. Chem. 1898, 27, 617). By careful regulation of the rate at which the air is forced through the ether, the bath can be adjusted to any point between room temperature and −15°.

When it is desired to find the molecular weight of a new substance, the question of the most suitable solvent arises. The choice is frequently limited by the solubility of the substance; it may be appreciably soluble in only one or two of the more common solvents. Apart from this, however, there are other considerations which must be taken into account. Extensive investigation has proved that with certain combinations of solvent and solute, the cryoscopic method gives abnormal values for the molecular weight of the dissolved substance. Pre-eminently is this the case when the solvent is water and the solute is an acid, a base, or a salt, in short, an electrolyte; under these circumstances, the value found for the molecular weight of the solute is abnormally low. On the other hand, the influence of substances containing the hydroxyl group (alcohols, acids, phenols, oximes) on the freezing point of hydrocarbons (benzene) and allied indifferent solvents, is such as to lead to abnormally high values for the molecular weight. The cryoscopic investigation of solutions of acetic acid in benzene indicates that the formula of the acid is more correctly represented by $(CH_3{\cdot}COOH)_2$ than by $CH_3{\cdot}COOH$. Again, while the molecular weight of alcohol in benzene is nearly normal in dilute solution, the value increases rapidly as the concentration of the alcohol rises. The combinations of solvent and solute which lead to abnormally high values of the molecular weight have been studied in detail by various workers (Auwers, Zeitsch. physikal. Chem. 1893, 12, 689; 1894, 15, 33; 1895, 18, 595; 1896, 21, 337; 1897, 23, 449; 1899, 30, 300; 1903, 42, 513, 629; Biltz, *ibid.* 1899, 29, 249; Robertson, Chem. Soc. Trans. 1903, 83, 1425; 1904, 85, 1617; 1905, 87, 1574; 1906, 89, 567). It should be noted that in cases also where the dissolved substance crystallises out along with the solvent, the depression of the freezing point is abnormally small, and the value of the molecular weight calculated therefrom is correspondingly high.

For the cryoscopic determination of the molecular weights of dissolved substances a method of moderate accuracy is sufficient, and an experiment may be carried out with a comparatively small quantity of liquid. The case is different with the problem of finding the exact depression of the freezing point for very dilute aqueous solutions—a problem to which much attention has been devoted because of its bearing on the theory of solution. It was early evident that the cryoscopic investigation of very dilute solutions involves special difficulties, for the discrepancies between the results obtained by different workers were very considerable. Thus the molecular depression for water, based on experiments with sucrose in which the actually observed depressions amounted only to about 0·05°, was found by Arrhenius to be 20·2°, by Raoult, 20·7°; by Jones, 21·8°; and by Loomis, 18·1°, instead of the theoretical value, 18·6°. Subsequent investigations (Nernst and Abegg, Zeitsch. physikal. Chem. 1894, 15, 681; Abegg, *ibid.* 1896, 20, 207; Wildermann, Phil. Mag. 1895, 40, 119; Proc. Roy. Soc. 1896, 251; Raoult, Zeitsch. physikal. Chem. 1898, 27, 617) have made it clear what conditions must be fulfilled if the freezing point depression for a dilute aqueous solution is to be determined with certainty to 0·001°. It will be sufficient here to indicate these conditions briefly.

As regards the thermometer, it is essential that a telescope be used for reading the position of the mercury, and that the bulb of the instrument be kept at about 0° during the whole of a series of experiments. The influence of alterations in the atmospheric pressure cannot be neglected, for it appears that a difference of 1 mm. mercury has about the same effect on a Beckmann thermometer as a temperature change of 0·0002°. On similar grounds, the thermometer must be immersed always to the same depth in solvent and solutions. It should be mentioned here that platinum resistance thermometers have been used in accurate cryoscopic work instead of the Beckmann instruments (*see* Chrustchoff, Compt. rend. 1900, 131, 883; 1901, 133, 955; Bedford, Proc. Roy. Soc. A, 1910, 83, 454). The difference between the freezing points of solvent and solution has also been determined thermoelectrically (Hausrath, Ann. Physik. 1902, [iv.] 9, 522).

The temperature of the cooling bath is a matter which has to be carefully considered, if the freezing point depression for a dilute solution is to be correctly determined. Suppose that in an experiment with the ordinary Beckmann apparatus the aqueous solution in the inner tube cools without freezing, it is obvious that the lowest temperature to which the solution can fall must be higher than that of the cooling bath, because of the heat conducted from the air to the solution through the thermometer, stirrer, and tube, and because of the heat generated by the stirring. This lowest temperature, which the contents of the freezing tube

tend to assume when no freezing takes place, is known as the *convergence temperature*. The difference between the convergence temperature and the temperature of the cooling bath varies, of course, with each apparatus; it decreases as the facility for heat exchange between the solution and the external air is lessened, and as the rate of stirring is diminished. Suppose now that the solution under examination has become supercooled, and that it has reached the convergence temperature. The introduction of a crystal of the solid solvent at this stage initiates the freezing process; heat is liberated and the temperature of the solution rises. Inasmuch, however, as the solution is no longer at the convergence temperature, there is an influence at work tending to lower the temperature of the solution, so that the latter never reaches its true freezing point: the maximum position reached by the mercury is only what may be called the *apparent* freezing point of the solution. Similarly, when the freezing point of the solution lies below the convergence temperature, an apparent freezing point is observed which is somewhat higher than the true freezing point. In both cases, the apparent freezing point lies between the true freezing point and the convergence temperature. In view of these considerations, it is necessary, in cryoscopic work of the most accurate kind, either to adjust the cooling bath so that the convergence temperature and the freezing point are practically the same, or to apply a correction to the apparent freezing point (*see* Raoult, *l.c.*; Nernst and Abegg, *l.c.*).

The freezing point of a solution is the temperature at which the solution and the solid solvent are in equilibrium, and in order that this equilibrium, and therefore the freezing point, may be well defined, it is essential that a considerable quantity of solid should be in contact with the solution. In the case of aqueous solutions, this has generally been effected by supercooling to the extent of 0·5° or 1·0°, and then introducing a crystal of ice. If this method is adopted, then a correction must be made for the change of concentration resulting from the separation of ice. Some workers, however, determine the freezing point by adding the cooled solution to a fairly large quantity of finely divided ice, and then observing the steady temperature shown by a thermometer immersed in the mixture (*see* Walker and Robertson, Proc. Roy. Soc. Edin. 1903, 24, 363; Richards, J. Amer. Chem. Soc. 1903, 25, 291; compare also Prytz, Ann. Physik. 1902, [iv.] 7, 882). In this method of procedure, equilibrium between the two phases is very rapidly established and the concentration of the liquid is ascertained by an analysis made subsequently to the determination of the freezing point.

It has already been pointed out that the freezing point depression is proportional to the number of dissolved units. The cryoscopic method may therefore be employed, not only in the determination of the molecular weights of dissolved substances, but also in the study of the question whether in a particular case a change in the number of dissolved units takes place. It is found, for instance, that the freezing points of potassium iodide solutions are not appreciably affected by the addition of iodine, which shows that the iodine must combine with the units already present in the solution (*see* Le Blanc and Noyes, Zeitsch. physikal. Chem. 1890, 6, 385; Paternò and Peratoner, Gazz. chim. ital. 1890, 21, 110). The cryoscopic method may similarly be employed in following the course of a reaction between dissolved substances which involves a change in the number of units, as for instance, the inversion of sucrose (*see* Kahlenberg, Davis, and Fowler, J. Amer. Chem. Soc. 1899, 21, 1).

J. C. P.

CRYPTOPINE *v.* VEGETO-ALKALOIDS.

CRYSOBERYL or **CHRISOBERYL** *v.* GLUCINUM.

CRYSTAL PONCEAU *v.* AZO- COLOURING MATTERS.

CRYSTAL VARNISH or **PAPER VARNISH** *v.* VARNISH.

CRYSTAL VIOLET *v.* TRIPHENYLMETHANE COLOURING MATTERS.

CRYSTALLIN *v.* PROTEINS.

CRYSTALLISATION. Crystals are often produced during the concentration of liquors in evaporating pans. Hand or mechanical scrapers are used for removing these crystals continuously. Such crystals are generally too impure for sale and are redissolved in sufficient hot water to produce a solution, which, after clarification by subsidence or filtration, will yield, in the crystallising pan, bright and marketable crystals. The temperature and concentration of the solution, to yield the best result, have to be determined for every substance. The mother liquor is run off and the crystals transferred to drainers or centrifugal machines to be dried before packing. In some instances, several repetitions of this treatment are made, and the crystals are washed with water or liquor after each treatment. The crystallising pans are made of materials which give the best economic result; either they resist the mother liquors or, if attacked, do not spoil the product by discolouration or too much impurity. Cast-iron tanks about 2 feet deep with bottoms sloping to the outlet and rounded corners, are common. Wooden tanks unlined or lined with sheet lead, zinc, tin, or other metal, are used largely. Some manufacturers suspend roughened strips of metal in the pans to which the crystals adhere. For rapid production, crystallisation by repose is now giving place in many industries to crystallisation in motion. The crystallising vessels are provided with circulating blades or with compressed air jets, so that the crystals as they form are prevented from adhering to the sides of the vessel, but remain suspended in the liquor, which, on complete cooling, flows directly to the centrifugal machines for the separation of the mother liquor. These crystals are purer and more convenient to handle than those obtained by repose methods. In the case of deliquescent substances and also in those instances where the mother liquor is sufficiently pure to make it unnecessary to purify by crystallisation, the liquor is concentrated in film evaporators so that only sufficient water remains in it to form the crystal. The liquor produced is run into drums and forms, on cooling, a solid block of crystals. In some works, the liquor is run into a jacketted worm conveyor so that the crystals which form, leave the apparatus in a loose state.

J. W. H.

CUBA BLACK *v.* AZO- COLOURING MATTERS.

CUBEBS CAMPHOR *v.* CAMPHORS.

CUBEBS, OIL OF, *v.* OILS, ESSENTIAL.

CUCUMBER. The fruit (really a berry) of *Cucumis sativus* (Linn.). König gives as the average composition:

Water	Nitrogenous matter	Fat	Other carbo-hydrates Sugar	Other carbo-hydrates Fibre	Ash
95·36	1·09	0·11	1·12	1·09	0·78	0·45

According to Wittmann (1901), cucumbers contain about 0·2 p.c. of pentosans.

Heinze (Zeitsch. Nahr. Genussm. 1903, 6, 529) observed that large cucumbers contain a higher proportion of sugar than small ones, but less nitrogenous matter. He gives as the mean composition:

	Water	Pro-tein	Fat	Glu-cose	Cane sugar	Other carbohy-drates	Fibre	Ash
Small	96·6	0·81	0·09	0·00	0·10	1·44	0·58	0·34
Large	95·8	0·67	0·09	0·66	0·09	1·60	1·65	0·42

The ash of cucumbers contains:

K_2O	Na_2O	CaO	MgO	Fe_2O_3	P_2O_5	SO_3	SiO_2	Cl
51·7	4·2	7·0	4·5	0·8	13·1	5·7	4·3	9·2

H. I.

CUDBEAR *v.* ARCHIL.

CULLEN EARTH or **COLOGNE EARTH** *v.* PIGMENTS.

CULLET *v.* GLASS.

CULM *v. Anthracite*, art. FUEL.

CUMENES. *Cumols.* The name *cumene*, originally applied to *iso*propylbenzene

$$C_6H_5{\cdot}CH(CH_3)_2$$

to indicate its connection with *cumic acid*, from which it was obtained by distillation with lime, is frequently employed as a generic term to denote any of the isomeric benzene hydrocarbons of the formula C_9H_{12}. Theory predicts the existence of eight of these, all of which have been found in coal-tar oil.

Propylbenzenes.

1. *Normal propylbenzene* (n- *cumene*)

$$C_6H_5{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3.$$

Present in coal-tar oil in fraction boiling at 153°–157° (Schultz and Perl, Ber. 1909, 3602). By the action of sodium on a mixture of bromobenzene and propyl bromide in ethereal solution (Fittig, Schäffer and König, Annalen, 149, 324). By the action of aluminium chloride on trimethylene bromide, propylbenzene and diphenylpropane (sym.) are formed, the latter of which, on further treatment, yields propylbenzene and cumene (Bodroux, Compt. rend. 132, 155). From benezene, aluminium chloride and propyl bromide, when kept at 0° (Heise, Ber. 1891, 768; Genvresse, Bull. Soc. chim. 9, [3] 219). From benzyl chloride, $C_6H_5{\cdot}CH_2Cl$ and zinc-ethyl (Paternò and Spiza, Ber. 10, 294). Liquid boiling at 159°(corr.), sp.gr. 0·867 at 15°/15° (Perkin, Chem. Soc. Trans. 1900, 274). Yields benzoic acid on oxidation with chromic acid.

2. *Isopropylbenzene* (*Cumene*)

$$C_6H_5{\cdot}CH(CH_3)_2.$$

Present in American petroleum (Maberry and Dunn, Amer. Chem. J. 18, 215). By distilling cumic acid $C_6H_4[CH(CH_3)_2]CO_2H(1, 4)$ with lime or baryta (Gerhardt and Cahours, Ann. Chim. Phys. [3] 1, 87). From benzal chloride $C_6H_5{\cdot}CHCl_2$ and zinc-methyl (Liebermann, Ber. 13, 46). Phenyl magnesium bromide reacts with acetone to give methylethenylbenzene, which, on hydrogenation, yields cumene (Tiffeneau, Compt. rend. 134, 845). From benzene and either *iso*propyl bromide or normal propyl bromide in presence of aluminium bromide (Gustavson, Ber. 11, 1251). Liquid boiling at 152·5°–153° (corr.); sp.gr. 0·8727, 7·9°/4°(Perkin, Chem. Soc. Trans. 1900, 275). Yields benzoic acid on oxidation with chromic acid.

Methylethylbenzenes (*Ethyltoluenes*). The three methylethylbenzenes are obtained by the action of sodium on a mixture of ethyl bromide or iodide with the corresponding bromotoluenes (ortho-, meta-, or para-).

1. *o-Methylethylbenzene*

$$C_6H_4(CH_3)(C_2H_5)(1, 2).$$

Liquid boiling at 158°–159°; sp.gr. 0·8731 at 16°. Dilute nitric acid oxidises it to *o*-toluic acid $C_6H_4(CH_3)CO_2H(1, 2)$.

2. *m-Methylethylbenzene*

$$C_6H_4(CH_3)(C_2H_5)(1, 3).$$

Liquid boiling at 158°–159°; sp.gr. 0·869 at 20°. Chromic acid oxidises it to *iso*phthalic acid $C_6H_4(CO_2H)_2$ (1, 3).

3. *p-Methylethylbenzene*

$$C_6H_4(CH_3)(C_2H_5)(1, 4).$$

Liquid boiling at 161°–162°; sp.gr. 0·8652 at 21°. Yields on oxidation *p*-toluic and terephthalic acids.

Trimethylbenzenes.

1. *Consecutive trimethylbenzene* (*Hemellitene*; *Hemimellithene*) $C_6H_3(CH_3)_3(1, 2, 3)$. By heating the calcium salt of *α-iso*duric acid

$$C_6H_2(CH_3)_3CO_2H$$

with lime. Liquid boiling at 168°–170° (Jacobsen, Ber. 15, 1857; 19, 2517).

2. *Unsymmetrical trimethylbenzene* (*pseudocumene*) $C_6H_3(CH_3)_3(1, 2, 4)$, occurs together with mesitylene in coal-tar (Beilstein and Kögler, Annalen, 137, 317), and is present in many petroleums (Poni, Chem. Zentr. 1906, i. 459). By the action of sodium on a mixture of either bromo-paraxylene or bromometaxylene with methyl iodide. In order to isolate it from coal tar, Armstrong recommends (Chem. News, 38, 5; Ber. 11, 1697) that the mixture of pseudocumene and mesitylene (*v. infra*) boiling between 160° and 170°, obtained from coal tar by fractional distillation, should be converted by treatment with an equal volume of concentrated sulphuric acid into sulphonic acids. The mixture of sulphonic acids, which separates as an oily layer on carefully adding water to the sulphuric acid solution, is heated with concentrated hydrochloric acid in a sealed tube for 1 hour at 100°. In this way, the mesitylene sulphonic acid is decomposed, regenerating mesitylene, whilst the pseudocumenesulphonic acid is not attacked. After separating the mesitylene the pseudocumenesulphonic acid is precipitated from the hydrochloric acid solution by sulphuric acid, purified by recrystallisation from dilute sulphuric acid and finally decomposed by heating with hydrochloric acid at 140°–150°, when it breaks up into pseudocumene and sulphuric acid. Jacobsen (Ber. 9, 256) treats the mixture of sulphonic acids with barium or calcium carbonate, which removes the excess of sulphuric acid and converts the sulphonic acids into

barium or calcium salts; transforms these by double decomposition with sodium carbonate into sodium salts; heats the latter with phosphorus pentachloride, with which they yield the sulphonic chlorides $C_9H_{11}\cdot SO_2Cl$; converts the chlorides into the sulphonamides

$$C_9H_{11}\cdot SO_2\cdot NH_2$$

by the action of ammonia; and separates the two isomeric sulphonamides by recrystallisation from alcohol, in which mesitylene sulphonamide is readily, pseudocumene sulphonamide only sparingly, soluble. The sulphonamides are then hydrolysed by heating with concentrated hydrochloric acid at 175°.

Another method proposed by Jacobsen (Annalen, 184, 199) is to separate the two sulphonic acids by fractional crystallisation; pseudocumenesulphonic acid *is* soluble with difficulty in sulphuric acid and crystallises out. On heating to its melting-point (110°) and passing in steam at a temperature of 250°, pure pseudocumene is obtained (*see also* Schultz and Herzfeld, Ber. 1909, 3602). Pseudocumene boils at 169·8° (corr.), 166° at 712 mm., and has sp.gr. 0·877 at 18° (Schultz and Herzfeld, *l.c.*). On oxidation with nitric acid, it yields two isomeric acids of the formula $C_6H_3(CH_3)_2CO_2H$—xylic acid and *p*-xylic acid—and a small quantity of the isomeric methyl*iso*phthalic and methylterephthalic acids $C_6H_3(CH_3)(CO_2H)_2$ (Bentley and Perkin, Chem. Soc. Trans. 1897, 165).

3. *Symmetrical trimethylbenzene* (*Mesitylene*) $C_6H_3(CH_3)_3$(1, 3, 5). In coal-tar oil, in fraction boiling at 157°–162° (Fittig and Wackenroder, Annalen, 151, 292; Schultz and Perl, Ber. 1909, 3602), and in American petroleum (Maberry and Dunn, Amer. Chem. J. 18, 215). By distilling acetone with sulphuric acid

$$3CO(CH_3)_2=C_6H_3(CH_3)_3+3H_2O$$

(Küster and Stollberg, Annalen, 278, 207; Meyer and Molz, Ber. 1896, 2831), or by dissolving allylene $CH_3C:CH$ in sulphuric acid and distilling with water $3CH_3\cdot C:CH=C_6H_3(CH_3)_3$ (Fittig and Schrohe, Ber. 8, 17). (On the isolation of mesitylene from coal tar and the method of separating it from pseudocumene, *v.* preceding paragraph.) Liquid boiling at 164·5°; sp.gr. 0·8768 at 4°/4° (Perkin, Chem. Soc. Trans. 1896, 1193). Dilute nitric acid oxidises it to mesitylenic acid $C_6H_3(CH_3)_2CO_2H$ and uvitic acid

$$C_6H_3(CH_3)(CO_2H)_2;$$

with potassium permanganate it yields uvitic acid and trimesic acid $C_6H_3(CO_2H)_3$(1, 3, 5).

CUMIDINES $C_9H_{13}N$. Of the sixteen isomeric cumidines which have hitherto been obtained, pseudo- or ψ-cumidine and mesidine are perhaps the most important. These bases are derivatives of pseudocumene and mesitylene respectively, the first of which is theoretically capable of yielding three isomeric ψ-cumidines, and the latter one cumidine only.

Pseudocumidine, *sym.-ψ-cumidine*

$(CH_3)_3C_6H_2\cdot NH_2$[$CH_3:CH_3:CH_3:NH_2$=1:2:4:5] can be obtained by nitrating pseudocumene with fuming nitric acid in the cold, and reducing the nitro- compound (m.p. 71°) with tin and hydrochloric acid (Schaper, Zeitsch. chem. [2] 3, 12). The base is prepared technically by digesting xylidine hydrochloride with methyl alcohol in an autoclave at 280°–300°, converting the crude product into the nitrate, separating the sparingly soluble nitrates by means of a centrifugal machine, washing the product with water and finally treating with an alkali. The mixture of bases consisting of cumidines and xylidines is then fractionated, and the portion distilling between 225°–245° is allowed to crystallise, and finally freed from non-crystallisable bases by pressure (Aktiengesellschaft für Anilinfabrikation, D. R. P. 22265). The cumidine so obtained contains mesidine and other impurities (Hofmann, Ber. 17, 1912; Engel, *ibid.* 18, 2229), but consists chiefly of Schaper's pseudocumidine (*cf.* Hofmann, *ibid.* 15, 2895) which can be prepared in the pure state by digesting *o*-4-xylidine [$NH_2:CH_3:CH_3$=1:3:4] or paraxylidine with methyl alcohol under similar conditions (Nölting and Forel, *ibid.* 18, 2680).

Properties.—Pseudocumidine crystallises in large, lustrous prisms, melts at 63° (Hofmann), at 68° (Auwers, Ber. 18, 2661), and boils at 234°. It is insoluble in water, but readily soluble in alcohol. The nitrate is characterised by being very sparingly soluble in water. Its acetyl derivative crystallises in compact white needles, melts at 161° (Edler, *ibid.* 18, 629; Nölting and Baumann), at 164° (Auwers) and boils above 360°. Pseudocumidine is used as a source of azo- dyes (D. R. PP. 3229, 1878; 22265, 1882).

***as*-ψ-cumidine** [$CH_3:CH_3:CH_3:NH_2$=1:2:4:6] has been prepared by Edler (*l.c.*). It melts at 36°.

ψ-cumidine [$CH_3:CH_3:CH_3:NH_2$=1:2.4:3] is obtained by digesting *o*-3-xylidine hydrochloride [$NH_2:CH_3:CH_3$=1:2:3] with methyl alcohol in an autoclave at 300° (Nölting and Forel; *cf.* Mayer, Ber. 20, 972). It boils at 240° Nölting and Forel), 236° and does not solidify at −15° (Mayer). Its acetyl derivative melts at 186°.

Mesidine [$CH_3:CH_3:CH_3:NH_2$=1:3:5:2] is obtained by treating mesitylene with nitric acid (sp.gr. 1·38) and reducing the nitro- derivative with tin and hydrochloric acid (Fittig and Storer, Annalen, 147, 3). It can also be prepared by digesting α-metaxylidine [$NH_2:CH_3:CH_3$=1:2:4] (Hofmann, Ber. 5, 715; 8, 61) or β-metaxylidine [$NH_2:CH_3:CH_3$=1:2:6] hydrochloride (Nölting and Forel) with methyl alcohol at 300°.

Properties.—Mesidine is a colourless liquid, which boils at 229°, and has a sp.gr. 0·9663. The acetyl derivative melts at 216° and crystallises in prisms.

***Iso*cumidine** [$CH_3:CH_3:CH_3:NH_2$=1:2:3:5], prepared by digesting the hydrochloride of γ-metaxylidine

[$NH_2:CH_3:CH_3$=1:3:5]

with methyl alcohol, at 300° (Nölting and Forel; Limpach, Ber. 1888, 644), melts at 67°–68°, boils at 245°, and yields an acetyl derivative melting at 163°–164°.

Para-aminopropylbenzene, formed by heating aniline, propyl alcohol, and zinc chloride at 280° for 8 hours (Louis, Ber. 16, 105; Francksen, *ibid.* 17, 1221), boils at 224°–226°. The acetyl derivative melts at 87°.

Orthoamino*iso*propylbenzene, *o*-cumidine, formed by heating aminocumic acid with baryta (Filetti, Gazz. chim. ital. 13, 379; *cf.* Constam and Goldschmidt, Ber. 1888, 1158), boils at 213·5°–214·5° at 732 mm. The acetyl derivative melts at 72°.

Para-amino*iso*propylbenzene, cumidine, formed by heating *iso*propyl alcohol, aniline, and zinc chloride at 260°–280° (Louis, Ber. 16, 111; *cf.* Nicholson, Annalen, 65, 58), boils at 216°–218°. The acetyl derivative melts at 102°–102·5°. By oxidation with sodium chlorate and potassium ferrocyanide in hydrochloric acid solution, cumidine yields a dyestuff of the aniline black series (Kirptischnikow, Chem. Zentr. 1906, i. 829). By treatment with cyanogen chloride in pyridine solution, condensation is effected and a dyestuff is produced (König, D. R. P. 155782; Chem. Zentr. 1904, ii. 1557).

Ethylorthotoluidine, prepared by treating orthotoluidine in ethyl alcohol with zinc chloride at 270° (Benz, Ber. 15, 1650), boils at 229°–230°. The acetyl derivative melts at 105°–105·5°, and boils at 313°–315°.

CUMIDINE RED *v.* AZO- COLOURING MATTERS.

CUMIN, OIL OF, *v.* OILS, ESSENTIAL.

CUPFERRON *v.* HYDROXYLAMINE.

CUPRISIN. Trade name for a preparation of cupric cyanide and potassium cyanide, used for the treatment of trachoma.

CUPRITE. Native cuprous oxide Cu_2O, crystallising in the cubic system. Brilliant, transparent crystals of a ruby-red colour (hence the name ruby-copper-ore) are not uncommon; sp.gr. 6·0. In the variety called *chalcotrichite*, the crystals are capillary in form, being enormously elongated in the direction of one of the cubic edges, and are loosely matted together in plush-like masses. Another variety, known as *tile-ore* (Ger. *Ziegelerz*), is earthy or compact and of a brick-red or brownish colour; it consists of an intimate mixture of cuprite and limonite, and has resulted from the alteration of copper-pyrites. Cuprite is sometimes of importance as an ore in the upper oxidised portions of copper veins. L. J. S.

CUPROSILICON, *Cuprous silicide* (*v.* COPPER).

CURARA. *Curare, Urari, Wourari, Wourali, Wourara.* Curara is the arrow poison of those tribes of South American Indians which inhabit the districts lying between the Amazon and the Orinoco. It was first brought to Europe by Sir Walter Raleigh, in 1595, and from that time to this its origin and preparation have been much discussed by travellers and botanists. A summary of the earlier observations of La Condamine, A. v. Humboldt and Bonpland, Waterton, Schomburgk, Castelnau, Weddell, Thirion, Jobert, Crévaux, and others is given in an examination of the subject by Planchon (Pharm. J. [3] 11, 469, 491, 529, 589, 693, and 754). It is shown that curara is an aqueous extract of a mixture of many plants, one of which is always a species of *Strychnos*, and gives to it the chief toxic power, whilst the remainder contribute those other qualities which render the extract suitable for the tipping of arrow heads. The method of preparation adopted by one tribe of Indians is described by Schomburgk (*ibid.* [3] 10, 646). The product differs somewhat with the locality in which it is prepared. Planchon distinguishes four varieties: the curara of the Orinoco, of the Upper Amazon, of French Guiana, and of British Guiana. The chief active ingredient in the preparation of the first is a *Strychnos* plant, closely allied to Schomburgk's *S. toxifera* (J. Pharm. Chim. [5] 5, 20), of the second, *S. Castelnæi* (Weddell), of the third, *S. Crevauxiana* (Baill.), and of the fourth, *S. toxifera* (Schomb.).

As seen in Europe, curara is a brown to black, nearly solid, or even brittle, extract. It has a bitter taste, and in its poisonous action it is related, though opposed, to strychnine. In medicine, it has been employed in the treatment of tetanus, epilepsy, and hydrophobia. It is best administered hypodermically in the form of aqueous solution (*cf.* Moss, Pharm. J. [3] 8, 421). The active part of curara is soluble in cold water, and constitutes three-fourths of the whole. This portion is nearly insoluble in alcohol, and quite insoluble in ether (Sachs, Annalen, 191, 255).

A more or less definite and active alkaloidal product of curara under the name *curarine* was described by Roulin and Boussingault (Ann. Chim. Phys. [2] 39, 24), A. v. Humboldt (*ibid.* [2] 39, 30), Pelletier and Pétroz (*ibid.* [2] 40, 213), Pryer (Zeitsch. Chem. 8, 381; Bull. Soc. chim. [2] 4, 238), Dragendorff (Zeitsch. Chem. [2] 3, 28), and Flückiger (Neues Rep. Pharm. 22, 65). Evidence of the same constituent in the root bark of *S. toxifera* has been obtained by Villiers (J. Pharm. Chim. [5] 11, 653). Pryer announced the discovery not only of crystalline salts of curarine, but of the base itself in a crystalline form, for which he proposed a formula. These results are, however, rendered doubtful by the experiments of Sachs (Annalen, 191, 254), which show that Pryer's crystalline curarine sulphate consisted of calcium phosphate, together with traces of carbonate and mechanically adhering curara, to which last its slight physiological activity is ascribed. Moreover, Pryer's formula, though derived from an undoubted platinum salt of curarine, is erroneous on account of the salt having suffered decomposition.

Sachs prepared a number of salts of curarine by precipitation from a solution of the acetate, which solution he obtained as follows. A solution of potassium mercuric iodide was added to a cold aqueous solution of curara, and the precipitate which formed, was collected. After washing, it was suspended in water and treated with sulphuretted hydrogen, which removes the mercury, while the alkaloid goes into solution. Lead acetate was then employed to separate the iodine, and finally the excess of lead was precipitated by sulphuretted hydrogen. The *platinum salt* obtained from this solution by the addition of platinic chloride and hydrochloric acid, is pale yellow, and has the composition

$$(C_{18}H_{35}N{\cdot}HCl)_2PtCl_4,$$

but changes rapidly with the formation of a violet-coloured compound of a different composition. The *gold salt* also quickly decomposes. Neither the sulphate nor the hydrochloride are crystallisable. The most stable and best-defined salt is the *picrate* $C_{18}H_{35}N{\cdot}C_6H_2(OH)(NO_2)_3$, from which Sachs deduces the formula $C_{18}H_{35}N$ for the free base. He also points out that the alkaloid exists in the extract combined with sulphuric acid.

Boehm (Ber. 20, Ref. 144) treats the aqueous solution of curara directly with platinic chloride, and by a series of operations, in which the presence of free mineral acid is avoided, obtains the *free base* as an amorphous yellow, or in

thicker layers orange-red, powder. If an aqueous solution of this powder, which has a green fluorescence, be evaporated with a little dilute acid, there result crystals of a physiologically inactive compound.

Further researches by Boehm (Arch. Pharm. 285, 660) show that the alkaloids of curara can be divided into two classes; (1) compounds similar to curine, partly crystalline and partly amorphous, soluble in water with difficulty and precipitated from solution by ammonia, in which the characteristic toxic effect of curara is shown very slightly or not at all; (2) amorphous yellowish-red substances easily soluble in water as curarine, not precipitated by ammonia, and showing the most marked toxic action. Para curara, which is imported in bamboo tubes and is the variety now usually met with in commerce, contains about 11–14 p.c. water, 12 p.c. ash, 12–15 p.c. *curine* $C_{18}H_{19}O_3N$, which is isolated by extracting the raw material with water, precipitating by aqueous ammonia and extracting with alcohol. It melts at 212°, and is obtained in crystals from benzene or alcohol with one molecule of the solvent or from methyl alcohol without alcohol of crystallisation. *Paracurarine* (*tubocurarine*) was obtained as a reddish-yellow substance which forms about 9–11 p.c. of raw curara. It is not identical with the previously known curarine, isolated from calabash curara. The latter kind, which was sent over in calabashes, used to be the common variety, but is now seldom met with. Earlier investigations, as a rule, refer to this. The active principle, *curarine*, consists of hard glistening garnet-red laminæ, decomposing and giving off a smell of trimethylamine when heated to 150°. A minute quantity of a second alkaloid was found to be present.

A third variety of curara occurs in the market in small jars of unburnt clay. This differs widely in respect to active principles from the other varieties. The following substances have been extracted from it: *protocurine*, colourless needles, which turn brown at 160° and melt, with decomposition, at 306°; *protocuridine*, colourless prismatic crystals, m.p. 274°–276°; and *protocurarine*, an amorphous red powder, more poisonous than the other curarines.

(For the physiological action of curara, *see* Nikolski and Dogiel (Pflügers Archiv. 47, 68); Frank and Voit (Zeitsch. Biol. 42, 309); Frank and Gebhard (*ibid.* 43, 117); Edmund and Roth (Amer. J. Physiol. 23, 28, 46).)

Curarine salts, according to Peliken (Ann. Chim. Phys. 44, 507), Pryer, Flückiger, and others, give a colour reaction with potassium dichromate and sulphuric acid similar to that of strychnine, but more permanent. Their behaviour towards solvents, especially water and benzene, serves to distinguish them from strychnine salts (Flückiger). Sachs obtained a red and not a blue colour by treating curarine salts with sulphuric acid, contrary to the statements of Pryer and Flückiger (*cf.* J. Soc. Chem. Ind. 1889, 476). (For extraction of curarine in poisoning cases, *cf.* Koch (Chem. Zentr. 1871, 219) and Salomon (Zeitsch. anal. Chem. 10, 454).)

A. S.

CURARE, CURARINE *v.* CURARA; VEGETO-ALKALOIDS.

CURCAS OIL, purging nut oil, physic nut oil (*Oleum infernale*), is obtained from the seeds of *Jatropha curcas* (Linn.), ('purging nut'), by hot expression. The seeds consist of 66 p.c. of kernels and 34 p.c. of husks. From the former there is obtained by extraction with ether 52 p.c. of oil of a pale colour, becoming yellow, with a reddish tint, on exposure to the air. Characteristic of the oil is its unpleasant odour, which assists in distinguishing curcas oil from other oils. Most prominent are the strong purgative properties of the oil, which are much more pronounced than those of castor oil. The oil belongs to the semi-drying oils; its liquid fatty acids consist of about equal proportions of oleic and linolic acids, as ascertained by the relative quantities of their oxidation products (viz. dihydroxystearic and tetrahydroxystearic acids). This oil is stated by Bouis to contain *iso*cetic acid, but the existence of this acid is doubtful.

Nearly related to the above-described oil are the oils obtained from the seeds of *Jatropha oligandra* (Mull.) and *J. multifida* (Linn.).

J. L.

CURCUMEÏNE *v.* AZO- COLOURING MATTERS.

CURCUMIN *v.* TURMERIC.

CURCUMINES *v.* AZO- COLOURING MATTERS.

CURCUPHENINE *v.* AZO- COLOURING MATTERS.

CURINE *v.* CURARA; VEGETO-ALKALOIDS.

CUSCAMINE, CUSCONINE *v.* VEGETO-ALKALOIDS.

CUSPARIA BARK. *Angostura bark*; *Carony bark.* (*Ecorce d'Angusture*, Fr.; *Angostura-Rinde*, Ger.) The bark of the *Cusparia febrifuga* (Hiemb.) or *Galipea cusparia* (St. Hilaire), a tree inhabiting the mountain districts drained by the Orinoco (*cf.* Bentl. a. Trim. 43). Confusion has sometimes occurred between cusparia and nux vomica bark. The two barks may, however, be readily distinguished by treatment with a drop of nitric acid, which either deepens the colour of the cusparia or gives it a bluish shade, while nux vomica, similarly treated, exhibits a blood-red colour. Several other barks have, from time to time, been substituted for true angostura. (For these, and the mode of detecting them, *v.* Pereira (Mat. Med. 3rd ed. 2, 1915); Maisch (Amer. J. Pharm. 1874, 50); Cazeneuve (Rép. de Pharm. 1874, 261); Oberlin and Schlagdenhauffen (Pharm. Zeit. 1878, 853).)

Among early analyses of cusparia, those of Pfaff and Fischer (Pereira) are the most important. These observers find in the dried bark 90 p.c. of lignin, together with gum, resins, volatile oil, and a peculiar bitter extractive. The bitter extractive, examined in 1833 by Saladin (J. de Chim. Méd. 9, 388), was found to contain a crystalline neutral principle to which the name *cusparin* or *angosturin* was given. An alkaloid, *angosturine* $C_{10}H_{40}NO_{14}$, differing from the cusparin of Saladin, was isolated by Oberlin and Schlagdenhauffen (J. Pharm. Chim. [4] 28, 263). It melts at 85°, is crystalline and bitter. It gives with sulphuric acid a red, and with sulphuric and nitric acids a green colour. Another *cusparine* was found in the bark by Körner and Böhringer (Gazz. chim. ital. 13, 363), who announce the discovery of several new basic and acid constituents. The cusparine of these chemists has the composition $C_{19}H_{17}NO_3$. It

is crystalline, and melts at 92°. It is sparingly soluble in ether, but soluble in alcohol. The sulphate, oxalate, and hydrochloride are only sparingly soluble in water. The platinum salt consists of orange-yellow crystals. Treated with potassium hydroxide, cusparine breaks up into a new crystalline *alkaloid* and an aromatic crystalline *acid*. The mother liquors from which cusparine is obtained contain another alkaloid, *galipeïne* $C_{20}H_{21}NO_3$. It consists of white needles, melting at 115·5°. The salts are more soluble than the corresponding salts of cusparine. The sulphate contains $7H_2O$. It melts at 50°, and at 100° breaks up into the sulphate of a *new alkaloid* and a crystalline *compound*, containing nitrogen, and melting at 196°. The platinum salt of galipeïne crystallises in prisms. A third *base*, melting at 180°, was also obtained. It is sparingly soluble in ether, but may be crystallised from alcohol. Its salts, when in solution, exhibit a blue fluorescence.

Angostura bark has been further examined by Beckurts and Nehring (Arch. Pharm. 229, 591), who have obtained four bases—galipine, galipidine, cusparine, and cusparidine, which are difficult to separate on account of their almost identical solubilities. *Galipine* $C_{20}H_{21}O_3N$ consists of pure white needles, melting at 115·5°. It dissolves readily in alcohol, chloroform, acetone, benzene, or ether, but is sparingly soluble in light petroleum. *Galipidine* $C_{19}H_{19}O_3N$ m.p. 111°, is very similar in properties to galipine. *Cusparine* $C_{20}H_{19}O_3N$ is the alkaloid most readily separated, owing to the sparing solubility of its salts. With concentrated sulphuric acid it gives a dull red, changing to a cherry-red colour. On treatment with fuming nitric acid, a yellow solution is obtained which, after evaporation and treatment with potash, becomes orange. Fröhde's reagent gives a brown solution, changing successively to violet, bluish-green, and deep blue (Beckurts, Arch. Pharm. 233, 410). *Cusparidine* $C_{19}H_{17}O_3N$, m.p. 78°, is very similar in properties to cusparine.

The bitter principle, angosturin, was found by Beckurts and Nehring to melt at 58°. These inquirers have also shown that the bark contains a glucoside which, however, was not obtained in a pure state; they also find that the essential oil previously studied by Herzog (Arch. Pharm. 93, 146; J. 1858, 444) and by Oberlin and Schlagdenhauffen (J. Pharm. Chim. [4] 26, 130), is present to the extent of 1·5 p.c.

A fifth alkaloid, *cuspareïne*, m.p. 154°, which does not form salts, has been isolated by Beckurts and Frerichs (Chem. Zentr. 1903, ii. 1010).

The bark of *Esenbeckia febrifuga*, which enters commerce under the name of angostura bark, has been examined by Hartwich and Gamper (Arch. Pharm. 238, 568).

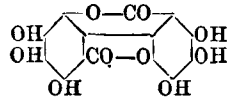
Cusparia is employed in medicine as a tonic in such derangements of the alimentary canal as dyspepsia, diarrhœa, and dysentery.

A. S.

CUTCH. *Terra japonica* (*v.* CATECHU).

CYANACETIC ACID *v.* MALONIC ACID.

CYANELLAGIC ACID. Cyanellagic acid $C_{14}H_6O_{10}$ is prepared by heating ellagic or flavellagic acid with 100 p.c. sulphuric acid at 185°–230° (Perkin, Chem. Soc. Proc. 22, 114), or with arsenic and sulphuric acids at 130°. It crystallises from pryidine in small yellow prismatic needles, and is soluble in strong alkaline solutions with a green yellow tint, changing to deep blue on dilution. The hexa-acetyl derivative $C_{14}O_{10}(C_2H_3O)_6$, forms colourless needles, melts at 330°–332°, and the hexabenzoyl compound, colourless needles m.p. 343°–345°. Cyanellagic acid is most probably dihydroxyellagic acid, and in this case possesses the following constitution :—



It dyes mordanted fabrics more readily than ellagic acid.

A. G. P.

CYANIDES. Compounds of the radicle cyanogen CN. The history of the cyanide industry begins with the discovery of Prussian blue by Diesbach in 1704 (H. Kopp, Geschichte der Chemie, 4, 369). While attempting to make Florentine lake by precipitating a mixture of cochineal infusion, alum, and ferrous sulphate with an alkali, he obtained a blue colour. The alkali used was potash, over which Dippel had distilled his animal oil, and Dippel recognised in this the source of the blue colouring matter. The new blue very quickly came into use in place of ultramarine, and in 1710 it was sold at one-tenth the price of the latter. The method of manufacture was a secret until 1724, when Woodward showed that the blue could be prepared by calcining blood with potassium carbonate and then treating the aqueous extract[1] with ferrous sulphate and alum, the greenish precipitate so obtained yielding Prussian blue when treated with hydrochloric acid.

Macquer, in 1752, showed that alum is not required, and that Prussian blue, when boiled with an alkali, yields ferric hydroxide and a soluble salt from which the blue can be regenerated. This salt, potassium ferrocyanide, was first obtained in the crystalline form by Sage in 1772.

The discoveries of Scheele, 1782–3 (Chemical Essays, London, 1786; reprinted 1901) Berthollet, 1790 (Annales de Chimie, 1790, 1, 30) and of Gay-Lussac, 1815 (*ibid.* 1815, 95, 156) cleared up the chemistry of Prussian blue and potassium ferrocyanide and of the closely related substances, cyanogen and hydrocyanic acid and their derivatives, and so laid the foundations of the industry.

Prussian blue was manufactured in Great Britain in 1770 by Bramwell & Co. of Newcastle; it sold then at 2 guineas per lb.; the price had fallen in 1815 to 10*s.* 6*d.*, in 1820 to 2*s.* 6*d.*, and in 1850 to 1*s.* 9*d.* Crystallised potassium ferrocyanide was first known in commerce about 1825, the price being 5*s.* per lb., although a solution had been sold previously (Graham, Reports of Juries, Exhib. of 1851, 1, 95).

The conversion of potassium ferrocyanide into potassium cyanide by fusion with potassium carbonate, was first described by F. and E.

[1] *Lixivium sanguinis*, or blood-lye, whence the German name of potassium ferrocyanide, '*blutlaugensalz*.'

Rodgers in 1834 (Phil. Mag. 1834 [3] 4, 91), but the simple cyanides were not used in any considerable quantity until the process of electroplating with gold and silver, from a cyanide solution, was discovered by J. R. and H. Elkington in 1840 (Eng. Pat. 8447, of 1840).

An interesting application of potassium ferricyanide was discovered by Sir J. Herschel in 1842 (Phil. Trans. 1842). Paper, treated with a solution containing ferric ammonium citrate and potassium ferricyanide, becomes blue when exposed to light, owing to the reduction of the ferric salt and consequent formation of Prussian blue. Paper sensitised in this way is used for the reproduction of engineering drawings.

A very remarkable attempt was made by Possoz and Boissière in the year 1843, to manufacture cyanides from atmospheric nitrogen; this is described under the heading POTASSIUM CYANIDE (p. 196).

The year 1860 witnessed three important developments in the cyanide industry. Gautier-Bouchard (A. W. Hofmann, Reports by the Juries, Inter. Exhib. of 1862, 59-63) began to produce prussiates from the spent oxide of the Paris gas works. A. Gélis (Eng. Pat. 1816, of 1860) synthesised them from carbon disulphide and ammonia; and Margueritte and de Sourdeval (Eng. Pat. 1171, of 1860) attacked the prolbem of the fixation of atmospheric nitrogen by means of barium oxide and carbon.

The existence of cyanogen compounds in coal gas was known in 1843, and possibly still earlier. E. Jacquemyns (Annalen, 1843, 46, 236, whose attention was drawn to them by H. Rose, says that he found none in gas lime, but obtained 0·75 gram of Prussian blue per litre from ammonia liquor. The purification of coal gas by means of iron oxide was introduced in 1847. Owing to the repeated use of the same quantity of oxide, the cyanogen compounds accumulate in it in a relatively concentrated form, and it was therefore naturally the first gas works product to be used in their manufacture. Prussian blue, made from spent oxide, was exhibited by Gauthier-Bouchard at the London Exhibition of 1862.

Both the process of Gélis and that of Margueritte and de Sourdeval were soon abandoned by their inventors; the recovery of cyanides from spent oxide, on the other hand, developed fairly rapidly, and, according to Dupré (Journ. für Gasbeleuchtung, 1884, 885), there were, in 1884, 10 works making prussiate by this means. The competition of the gas works prussiate, together with the increasing cost of nitrogenous organic matters (which were being used more and more as fertilisers), soon displaced the old process in Germany. In the United States of America, it appears to have held its own somewhat longer; the returns of the U.S. Census for 1900 (Bulletin No. 210, 31, 1902) show 18 works engaged in the manufacture of cyanides with a joint annual production of 2752 tons of yellow prussiate, almost entirely made from hoofs, horns, and scrap leather, only 1200 tons of spent oxide having been used.

Between 1875 and 1885, the sulphocyanides, especially the tin and aluminium salts, appear to have been used in calico printing instead of the acetates (Bertelsmann, Die Technologie der Cyanverbindungen, 303), and Gélis' synthesis was taken up and improved by Günzburg and Tcherniac (Eng. Pat. 1148, of 1878; 1359, of 1879; 1261, of 1881), but without financial success.

In 1887, J. S. MacArthur, R. W. and W. Forrest (Eng. Pat. 14174, Oct. 19, 1887; 10223, of 1888) patented their process for the extraction of gold and silver from their ores by means of a dilute solution of a cyanide. The process was carried out by allowing a solution containing 0·25 p.c. or less of potassium cyanide to percolate through the ore, which was usually ground to pass a sieve with 40 or 60 holes to the linear inch. The gold is dissolved in the form of potassium aurocyanide, and is recovered from the solution by passing it through a mass of zinc shavings. The process was first put into practice at Karangahake, New Zealand, in 1889, and near Johannesburg, Transvaal, in 1890. The success of these installations led to a very rapid adoption of the process in all the gold-producing countries of the world.

Prior to the introduction of this process, the cyanide industry was quite a small one. The world's consumption of potassium cyanide (produced exclusively from ferrocyanide by the Rodgers process) (F. Roessler, V. Internationaler Kongress für Angewandte Chemie, Berlin, 1903, 1, 638) did not exceed 50-70 tons per annum (G. Beilby, J. Soc. Chem. Ind. 1898, 134) and that of yellow prussiate was probably under rather than over 5000 tons (worth together about 325,000*l.*).

Ten years later, just before the Transvaal War, the European production of potassium cyanide was estimated by Beilby (V. Inter. Kongress Angew. Chem. Berlin, 1903, 1, 630) as 5500 tons, adding the American production of about 1000 tons (U.S. Census Bulletin, No. 210, 31, 1902), we arrive at a total production of 6500 tons. Since then the world's output of cyanide has continued to increase, although at a relatively slower rate. The production of ferrocyanides, on the other hand, has remained comparatively stationary, the outlets for these substances in paint making, dyeing and calico printing, not permitting any great expansion.

The increased quantities of potassium cyanide required by the gold-mines were at first supplied by fusing potassium ferrocyanide with potassium carbonate, and very soon afterwards by E. Erlenmeyer's process (Ber. 1876, 1840), in which dry prussiate and metallic sodium are used: $K_4Fe(CN)_6+2Na=2NaCN+4KCN+Fe$. Synthetic processes producing cyanide direct without the intervention of prussiate, were also introduced, no less than 104 patents connected with cyanides being applied for during 1889-1898, and 129 from 1899-1908. The processes which have worked with some measure of success are tabulated below:—

Process	Where worked	Began production in
Siepermann	Stassfurt	1892
Beilby	Glasgow	1892
Castner	Great Britain, Germany, U.S.A.	1900
Raschen	Runcorn	1898
Readman	Leven (Scotland)	1899-1906[1]
Bueb ('Schlempe')	Dessau	1902

These processes are described fully below.

[1] Ceased producing.

Potassium cyanide, as used in electroplating, was a material having the appearance of unglazed porcelain, and containing from 30 to 70 p.c. of KCN, together with large quantities of carbonate and cyanate. The material supplied to the gold-mines in the early days of the gold-extracting process was a black mass containing some 75 p.c. of KCN, and all the iron and carbon liberated by the decomposition of the ferrocyanide. This was replaced by the pure white crystalline product of the Erlenmeyer process, which contained about 2 molecules of KCN to 1 molecule of NaCN, the cyanogen content being about 40 p.c., equivalent to 98–100 p.c. of KCN. Shortly after the introduction of the Castner process, in 1900, solid cakes of pure white crystalline sodium cyanide, containing 97 p.c. to 98 p.c. of NaCN (equivalent to 129–130 p.c. of KCN), became an article of commerce, and this is at present the form in which the greater part of the cyanide employed in gold-extracting is used.

The time-honoured yellow prussiate of potash has also been replaced to a very large extent by the sodium salt which is quite easily prepared by the more recent methods of extracting the hydrocyanic acid from coal gas by special cyanogen washers (*see* p. 185).

The application of hydrocyanic acid as an insecticide, which was introduced in California in 1903, promises to become of some importance. Fruit trees (especially orange trees) are covered with a tent under which hydrocyanic acid is produced by mixing sodium cyanide and sulphuric acid (W. F. Reid, Journ. of Gas Lighting, 1904; *also* J. Soc. Chem. Ind. 1903, 22, 1330).

Another possible application which may be mentioned is in case-hardening iron; immersion in fused cyanide produces a very hard skin on mild steel, and ferrocyanides have long been used for this purpose in ordinary workshop practice.

Potassium ferrocyanide $K_4Fe(CN)_6,3H_2O$ (Yellow prussiate of potash, Ger. *Blutlaugensalz*).

The method of manufacture from nitrogenous organic matter is now only of historical interest.

The sources of nitrogen were horn, dried blood, hair, waste wool, and feathers (15–17 p.c. N), woollen rags (10–16 p.c. N), pigs' bristles (9–10 p.c. N), and old leather (4·5–7 p.c. N). These materials were sometimes charred before use, about 80 p.c. of the nitrogen being driven off in the form of ammonia, hydrocyanic acid, and a complicated mixture of nitriles and organic bases.

The process was carried out at first in pear-shaped, cast-iron muffles, which were replaced later by reverberatory furnaces, the beds of which were formed of cast-iron pans, 5 feet long, 3 feet wide, 4 inches deep, and about 2 inches thick. A charge of 2 cwt. of potash (usually made up of 2 parts of the 'blue salt' recovered in a later stage of the process, and 1 part of fresh potash) was put into the pan and fused with 18–20 lbs. of iron turnings; 2 cwt. of the dry nitrogenous materials were then stirred in gradually (2·5 to 3 cwt. of *charred* material could be added without making the mass too pasty). The temperature was then raised in order to complete the reaction, and the melt ladled out into iron moulds. After solidification, it was broken up and digested for 24 hours with water at 50°–60°, and finally extracted completely with boiling water. The solution obtained contained potassium ferrocyanide, sulphocyanide, carbonate and sulphide. It was evaporated to sp.gr. 1·28, and allowed to crystallise. Further evaporation yielded a second crop of impure crystals, the mother liquor of which was evaporated to dryness, leaving a mixture of potassium carbonate and sulphide, known as 'blue salt' which was returned to the fusion pan.

The black insoluble residue left from the extraction of the 'metal,' as the product of the fusion was called, contained considerable quantities of potassium, mainly in the form of potassium ferrous sulphide and of double potassium, calcium, and aluminium silicates.

The quantity of 'metal' produced was very little greater than the weight of potash used, and 4 charges were put through in 24 hours, but practice varied considerably: C. Karmrodt (Wagner's Jahresber. 1857, 3, 139) speaks of 6 charges of 500 lbs. each as the normal output of a pan in 24 hours.

The yield of ferrocyanide was seldom more than 20 p.c. of the quantity theoretically obtainable from the nitrogen in the materials used when they were not previously charred. Using charred materials, as much as 57 p.c. of the remaining nitrogen was converted into ferrocyanide, corresponding with a yield of about 12 p.c. on the nitrogen originally present.

The quantity and composition of the black residues varied greatly with the kind of organic matter used. The main constituents were carbon (4–9 p.c.), ferrous sulphide, iron, and inorganic substances derived from the ash of the animal matters and adhering dirt, the principal being silica, lime, alumina, and phosphoric acid. The quantity of potassium combined with these substances in an insoluble form was considerable. According to Karmrodt (Wagner's Jahresber. 1857, 3, 139), 100 parts of 'metal' made (1) from horn gave 18·7 p.c. of dry residue, containing 12·2 p.c. of K_2O; (2) from rags, 28·3 p.c. of residues, with 16·7 p.c. K_2O; (3) from leather, 35·1 p.c. of residue, with 10·2 p.c. K_2O. These quantities represent about 4½, 9, and 7 p.c. of the potassium contained in the original charge, and since only some 10 p.c. of this is converted into ferrocyanide at each operation (R. Brunquell, Wagner's Jahresber. 2, 102, 1856), the loss of potash in the residues appears to have been from 45 to 90 p.c. of that usefully employed. Potash was also carried away with the flue gases. The iron pans survived several hundred operations.

The theory of the process was first given by Liebig (Annalen, 1841, 38, 20). Scheele (Chemical Essays, London, 1786; reprinted 1901) had already shown that *lixivium sanguinis* is essentially a solution of potassium cyanide and that the addition of a ferrous compound is necessary to convert it into prussiate. Liebig confirmed this by extracting the 'metal' with alcohol, which dissolves out potassium cyanide, leaving a residue from which no ferrocyanide can be obtained. He attributed the formation of the cyanide partly to the action of ammonia (formed by destructive distillation of the organic matter)

on carbon, $C+NH_3=HCN+H_2$, and partly to the action of potassium on the nitrogenous residue of carbon. It may be remarked that the temperature of the fusion could not have exceeded 1000°, since cast iron melts about 1100°, and the pans withstood some hundreds of fusions. The temperature, too, was lowered by the addition of the organic matter, occasionally sufficiently to cause the charge to solidify, so that the reaction between ammonia and carbon, which requires a temperature of about 1000°, could not have occurred to any great extent. The direct action of ammonia on potassium carbonate (p. 193) would, however, take place, although, the ammonia being evolved on the surface of the mass, the conditions were not favourable to it. As to the second of Liebig's reactions, the writer has found that potassium is not formed from a mixture of charcoal and potassium carbonate below about 1200°, certainly not at 1000°, so that the greater part of the cyanide must have been formed by the action of potassium carbonate itself on the nitrogenous charcoal. The rôle of sulphur in the process was explained by Liebig thus: potassium sulphate, which is always present in the potash, is reduced by carbon to sulphide, carbonate, and polysulphide. The latter dissolves iron, forming a double sulphide of iron and potassium which, when the product is lixiviated, dissolves in the potassium cyanide solution thus:

$$6KCN+FeS=K_4Fe(CN)_6+K_2S.$$

If insufficient iron is present in the fusion, the polysulphide is not entirely decomposed, and potassium sulphocyanide is also formed. R. Hoffmann (Annalen, 1860, 113, 81) investigated the behaviour of the sulphur compounds in the process in some detail, and found that the sulphur of potassium sulphide is rapidly and completely removed by iron alone in the fusion process, and that the same is true of potassium sulphate in presence of carbon. When organic matters are added to the sulphur-free melt, however, sulphocyanide is produced in proportion to the quantity added. Hoffmann, therefore, attributes its formation to the organic sulphur.

The behaviour of potassium sulphocyanide in the fusion is not clearly understood. Hoffmann found that it is completely decomposed by fusion with excess of potassium carbonate, yielding cyanate and sulphide;[1] but if the mixture is again heated with carbon, the sulphocyanide is regenerated. It appears, therefore, that, under the conditions of the process, sulphocyanide is not decomposed.

A part of the sulphide of iron formed is present in the form of a potassium ferrous sulphide, $FeS{\cdot}xK_2S$, which dissolves in hot water to a dark-green, colloidal solution which is coagulated by cooling or by adding excess of potassium carbonate. Another part is probably present in the form of the crystalline potassium ferric sulphide $K_2S{\cdot}Fe_2S_3$, obtained by K. Preis (J. pr. Chem. 1869, 107, 10), by fusing together finely divided iron, potassium carbonate, and sulphur. He found that the crystalline sulphide was formed at very high temperatures, and the amorphous one, yielding the green solutions, at lower temperatures.

The reaction between potassium cyanide and ferric sulphide

$$13KCN+Fe_2S_3=2K_4Fe(CN)_6+KSCN+2K_2S$$

would give a ratio of cyanogen in the form of sulphocyanide to cyanogen in the form of ferrocyanide of 1:12, whilst Hoffmann, in 10 experiments, found ratios varying from 1 : 5 to 1 : 18.

The improvements in the process which were proposed, aimed at saving the ammonia evolved in the early stages by distilling the organic matters separately and passing the ammonia through a red-hot mixture of potash and charcoal (Brunquell, Wagner's Jahresber, 1856, 2, 102), or a similar mixture with iron added (Karmrodt, *ibid.* 1857, 3, 139), or over red-hot charcoal forming hydrocyanic acid which was to be absorbed, together with the unchanged ammonia, in a solution of ferrous sulphate (Brunquell). These proposals, unfruitful at the time, are interesting as foreshadowing processes which came into successful operation nearly half a century later.

The commonly accepted view that cyanogen compounds are more easily produced from potash than from soda, is not entirely in accordance with the older experimental evidence. The truth appears to be that equally good results can be obtained with sodium carbonate under suitable conditions, but the conditions are not so easily realised.

L. Possoz (Compt. rend. 1858, 47, 209) obtained, under manufacturing conditions, 5 parts of sodium prussiate, instead of 25 parts of the potassium salt, from 100 parts of horn. R. Hoffmann (Annalen, 1860, 113, 81), using a very high temperature and sodium carbonate, got the equivalent of 11 parts of potassium ferrocyanide from 100 parts of woollen rags, against 10 to 14 parts with potash, and S. Tanatar (Dingl. poly. J. 1880, 237, 234) obtained the results tabulated below, as the means of 3 to 5 experiments:—

Blood charcoal	K_2CO_3	Na_2CO_3	NaCl	$CaCO_3$	Prussiate obtained
10	25	—	—	—	2·15
10	—	25	—	—	0·2
10	—	5	25	—	2·17
10	—	5	25	3	2·3

Ferrocyanides from coal gas. The coal used in the manufacture of illuminating gas may be taken to contain from 1 to 1·9 p.c. of nitrogen (Drehschmidt, Journ. für Gasbeleuchtung, 1904, 677). When the coal is distilled, a part of this nitrogen passes into the gas in the form of ammonia, hydrocyanic acid and free nitrogen, a small part is found in the tar, and the remainder in the coke. The relative quantities of the nitrogen in these products vary between wide limits, being influenced by the nature of the coal, the amount of moisture in it, the temperature of distillation, and the kind of retort used. In order to give an approximate idea of the order of magnitude of the quantities involved, it may be stated that under average conditions about 15 p.c. of the nitrogen is found as ammonia, 2·5 p.c. as hydrocyanic acid, and 48 p.c. in the coke (Drehschmidt, Journ. für Gasbeleuchtung,

[1] I can confirm the accuracy of this observation. Equal molecules of potassium carbonate and sulphocyanide were fused together in a closed aluminium crucible at 500°–580° for 1½ hours, a little more than half of the materials had reacted in accordance with the equation $KSCN+K_2CO_3=KCNO+K_2S+CO_2$.—T. E.

1904, 677; Vivian Lewes, quoted from Chief Inspector of Alkali Works, 43rd Rep. 1906, 58); this gives a yield of 1·6 lbs. of hydrocyanic acid or 4·6 lbs. of sodium ferrocyanide crystals per ton of coal distilled. When the gas is purified by means of ammonia scrubbers and iron oxide purifiers, about one-third of the hydrocyanic acid is condensed along with the ammonia in English works (Chief Inspector of Alkali Works, 43rd Rep. 1906, 61), but less in many German works, where less water is used in the scrubbers (W. Bertelsmann, Technologie der Cyanverbindungen, 171), and from 50 to 70 p.c. in the iron oxide purifiers, the remainder passing away in the gas, where it is a source of damage to meters and gas holders. When lime is used for purification, the cyanide is mainly caught as sulphocyanide, and in such small quantity (the lime being only used once) that the spent lime is worthless as a raw material for cyanide making.

The gas, as it leaves the retorts, contains the whole of its cyanogen in the form of hydrocyanic acid (Chief Inspector of Alkali Works, 43rd Rep. 1906, 33), which is formed by the action of ammonia on red-hot carbon, thus: $NH_3+C=HCN+H_2$. The hydrocyanic acid is reconverted by water vapour at high temperatures into ammonia (Carpenter and Linder, J. Soc. Chem. Ind. 1905, 24, 63): $HCN+H_2O=NH_3+CO$, so that moisture in the coal diminishes the yield of hydrocyanic acid. This is doubtless the reason that much smaller quantities of hydrocyanic acid are found in the gases of coke ovens, where the coal is distilled in a much wetter condition.

The treatment of gas liquor is discussed under the heading *Sulphocyanides* (p. 200).

Spent oxide. The hydrated oxide of iron first used in gas purification was made by mixing ferrous sulphate and slaked lime, sawdust being added to increase the porosity (Laming, Eng. Pat. 11944, of 1847), natural iron ores were introduced by Howitz in 1870. Sulphuretted hydrogen is absorbed, yielding a mixture of ferrous and ferric sulphides which is regenerated by exposure to air and moisture, free sulphur and ferrous and ferric hydroxide being produced. Ferrocyanide is formed from the ferrous hydroxide and hydrocyanic acid, and then converted into Prussian blue by interaction with the ferric iron. Sulphocyanides are also formed in very variable amount, doubtless by the interaction of hydrocyanic acid and ammonium polysulphide. Since ammonia, sulphuretted hydrogen, and free sulphur are always present in the purifiers, it is obvious that polysulphides of ammonium can always be formed; it appears to be generally allowed, however, that sulphocyanide is only produced in large amount when the mixture becomes warm, as, for example, when the regeneration proceeds rapidly in a large mass of material. The spent oxide finally contains 30 to 40 p.c. of sulphur (or more), soluble ammonium salts and Prussian blue, in addition to tar and iron oxides. Good material contains 11 to 12 p.c. of Prussian blue, calculated on the air-dried substance, whilst ammonium sulphocyanide varies from traces to 10 p.c.

As already mentioned, prussiates were first produced from spent oxide by Gautier-Bouchard about 1860. Ammonium salts were first removed by washing with water; the residue was then mixed intimately with sufficient lime to convert the Prussian blue into calcium ferrocyanide and the mixture submitted to systematic lixiviation with cold water. This operation must be done in the cold, because otherwise calcium polysulphide is produced from the lime and free sulphur, and this converts the ferrocyanide into sulphocyanide. The calcium ferrocyanide was converted into the potassium salt by means of potassium carbonate, and the sulphur in the extracted residue burned to sulphur dioxide and converted into sulphuric acid (A. W. Hofmann, Reports by the Juries, Inter. Exhib. of 1862, 59–63). This process contains the essential features of all those which have since been worked successfully.

T. L. G. Bell (Eng. Pat. 257, of 1868) proposed to extract the sulphur with carbon disulphide, and, after removing soluble ammonium salts with water, to boil the residue with lime. In order to obtain a pure product, the solution was then acidified and precipitated by the addition of ferric chloride, the Prussian blue being then converted into potassium ferrocyanide. The preliminary extraction of the sulphur has occasionally been carried out, but it is difficult to separate the sulphur from the tar which is extracted along with it. In spite of the great difficulty of filtering and washing Prussian blue, this method of purification appears to have been fairly generally used up to the year 1883, when Kunheim and Zimmermann (Eng. Pat. 3342, of 1883) described two new methods.

In the first, the ammonia is only partially removed from the spent oxide by the preliminary washing, enough being left behind to produce the double salt $Ca(NH_4)_2Fe(CN)_6$. The extraction with lime then yields an ammoniacal solution of calcium ferrocyanide, which, when neutralised with hydrochloric acid and heated to 80°, deposits the very sparingly soluble calcium ammonium ferrocyanide, which is comparatively easily filtered and washed.

By the second method, the solution of calcium ferrocyanide, obtained by following Gautier-Bouchard's original procedure, is treated with a solution of potassium chloride which precipitates the double salt $CaK_2Fe(CN)_6$ in minute crystals, which are very readily washed and are then converted into potassium ferrocyanide by boiling with potassium carbonate. By this means one half of the potassium carbonate is replaced by the cheaper chloride, and a very pure product is obtained (Franz Bössner, Die Verwerthung der Ausgebrauchten Gasreinigungsmassen, 1902). From the calcium ammonium salt, sodium prussiate is readily obtained.

During the decade 1885 to 1895, the spent oxide of the gas works was the principal source of prussiates; its importance, however, has been diminished by the introduction of the more efficient wet methods of recovering the hydrocyanic acid.

The first practicable proposal of this kind was made by O. Knublauch (Eng. Pat. 15164, of 1887). Coal gas was to be scrubbed with a solution of the oxide, hydroxide, carbonate, or sulphide of ammonium, or of an alkali or alkaline-earth metal containing the hydroxide or

carbonate of iron, zinc, or manganese in suspension. The process did not succeed at the time, probably for commercial reasons. The very similar process of Foulis (Eng. Pat. 9474, of 1892; Foulis and Holmes, Eng. Pat. 15168, of 1895), has since been introduced at several gas works with satisfactory results. In this process, the reagent required is prepared by precipitating a ferrous salt with sodium carbonate. The washed precipitate (a partially oxidised mixture of ferrous carbonate and hydroxide) is suspended in a solution of sodium carbonate and the gas passed through it in a rotary scrubber. Foulis wished to obtain the whole of the ferrocyanide in solution in the form of the sodium salt, and therefore placed the cyanogen washer after the ammonia scrubbers because, in presence of ammonia, a double ammonium ferrous ferrocyanide is formed which is only decomposed by sodium hydroxide, but not by the carbonate. At the Hague gas works, however, this order was reversed in order to catch the hydrocyanic acid which is otherwise condensed along with the ammonia (Rutten, Journ. of Gas Lighting, 1902, 80, 879; Jorrisen and Rutten, Journ. für Gasbeleuchtung, 1903, 716). The saturated liquor from the cyanide washer contains Prussian blue and potassium and ammonium ferrous ferrocyanides in suspension and potassium ferrocyanide and ammonia in solution (potassium carbonate is used instead of the sodium salt). This mixture is filter-pressed and the solution distilled to separate the ammonia and then evaporated *in vacuó* and crystallised. The press cake is boiled with caustic potash and the ammonia collected, the residual iron oxide returning to the cyanide washer, and the solution of ferrocyanide going to the evaporating plant.

In another set of proposals, the use of an alkali other than the ammonia of the gas is dispensed with, the crude coal gas being simply washed with a solution of ferrous sulphate. Since ammonia and sulphuretted hydrogen are present in much larger quantities than hydrocyanic acid, the ferrous sulphate is soon converted into a suspension of ferrous sulphide in a solution of ammonium sulphate, and the subsequent changes may be regarded as due to the action of a solution of ammonium cyanide on ferrous sulphide. If a large excess of the latter is present, the main product is ferrous ferrocyanide $Fe_2[Fe(CN)_6]$; as the ferrous sulphide is used up, ammonium ferrous ferrocyanide $(NH_4)_2Fe[Fe(CN)_6]$ is formed in increasing quantities, and finally, when but little FeS remains, ammonium ferrocyanide is found in solution (Feld, Journ. für Gasbeleuchtung, 1904, 132).

The earlier patentees of processes based on these reactions attempted to obtain the ferrocyanide in a soluble form by using a dilute solution of a ferrous salt, and so having a large excess of ammonia present (Rowland, Eng. Pat. 22347, of 1891; Lewis and Cripps, Eng. Pat. 20883, of 1896; Schröder, Eng. Pat. 19849, of 1898; Teichmann, Eng. Pat. 12485, of 1899), but since insoluble compounds are always formed to some extent, it appears to be easier to obtain all the ferrocyanide (or the greater part of it) in the insoluble form by using a saturated solution of ferrous sulphate, and so having a large excess of iron present as first proposed by Bueb (Eng. Pat. 9075, of 1898). Bueb's process has been adopted by a considerable number of gas works. It is said to absorb 98 p.c. of the hydrocyanic acid in the gas, yielding a mud containing 6–7 p.c. of ammonia and cyanogen compounds, equivalent to 18–20 p.c. of yellow prussiate of potash. A small part of the ferrocyanide is in solution. This is precipitated by boiling the mixture with ferrous sulphate; the precipitate is then filtered off and treated with lime, the subsequent operations being the same as those already described when dealing with spent oxide.

Manufacture of Prussiates from Sulphocyanides.

A. Gélis (Eng. Pat. 1816, of 1860) was the first to manufacture potassium ferrocyanide by heating potassium sulphocyanide with iron. He heated dry potassium sulphocyanide with iron, made by reducing the oxide, at a dull-red heat in a closed vessel. He states that too high a temperature leads to considerable loss. The fusion process yields a mixture of potassium cyanide and ferrous sulphide which gives potassium ferrocyanide, when treated with water in the same way as the 'metal' of the old process (A. W. Hofmann, Reports by the Juries, Inter. Exhib. of 1862, 59–63). Mr. G. Beilby has informed the writer that he made considerable quantities of potassium ferrocyanide by this process about the year 1880. Potassium sulphocyanide was heated with iron turnings in air-tight iron retorts and, after cooling sufficiently, the product was extracted with water in the retort itself, without coming in contact with air. In this way the only serious difficulty of the process, which is due to the extreme proneness to oxidation of the fusion product, is avoided and satisfactory yields obtained.

The process was taken up again in 1878 by Günzburg and Tcherniac (Eng. Pat. 1148, of 1878; 1359, of 1879; 1261, of 1881). They dried the sulphocyanide by fusing it at 300°, and then mixed it intimately with the oxide-free iron by grinding them together. The mixture was heated in iron boxes with closely fitting covers at 445°, the vapour of boiling sulphur being used to obtain a constant temperature. After working for two or three years, the process was given up, but it was revived for the third time in 1894 by the United Alkali Co., Ltd. (Hetherington and Muspratt, Eng. Pat. 5830, of 1894), and by the British Cyanides Co., Ltd. (Crowther, Rossiter, Hood and Albright, Eng. Pat. 8305, of 1894). The patent specifications of Hetherington and of Crowther add but little to the information given above. In both cases, some 20 to 30 p.c. excess of iron is used, and the temperature is almost the same as that recommended by Günzburg and Tcherniac. Crowther says that mere fusion is insufficient to dry the sulphocyanide: a current of an indifferent gas must be passed through it for some time. Conroy (J. Soc. Chem. Ind. 1896, 15, 12) was able, in a small scale experiment, to convert 76·8 p.c. of the sulphocyanide used into ferrocyanide (leaving 18·2 p.c. unchanged) by means of Hetherington's method. The process has been worked by the British Cyanides Co. at Oldbury since 1894 (Brussels Exhib. 1910, Catalogue of British Chem. Section, 105).

The conversion of sulphocyanides into ferrocyanides is also possible in aqueous solution. Sternberg (D. R. P. 32892, of 1882), found that by heating a solution of potassium sulphocyanide with double the theoretical quantities of iron filings and ferrous hydroxide under pressure at 110°-120°, about 80 p.c. of the material could be converted into ferrocyanide in accordance with the equation

$$6KCNS+6Fe+Fe(OH)_2=6FeS+K_4Fe(CN)_6+2KOH.$$

G. R. Bower (Eng. Pat. 361, 1896) succeeded in removing the sulphur from ferrous sulphocyanide by means of copper in a similar way: $Fe(CNS)_2+Cu=2CuS+Fe(CN)_2$. Conroy (Conroy, Hurter, and Brock, Eng. Pat. 3867, of 1896; J. T. Conroy, J. Soc. Chem. Ind. 1898, 17, 98) then found that a mixture of a soluble sulphocyanide and a ferric or ferrous salt would do as well as pure ferrous sulphocyanide, and also that the sulphur is more rapidly removed by finely divided iron than it is by copper. Using very finely divided iron, the reaction takes place quantitatively in 5 to 6 hours at a temperature of 135°-140° and a pressure of 50 to 60 lbs. per square inch, in accordance with the empirical equation $Fe(CNS)_2+2Fe=Fe(CN)_2+2FeS$. (Sodium or potassium sulphocyanide is acted on by iron under similar conditions very slowly and incompletely.) The black mud produced is either boiled with caustic alkali to decompose the ferrous ferrocyanide, or the ferrous sulphide is first dissolved in hydrochloric acid. The latter course is to be preferred, owing to the fact that ferrous sulphide combines with the alkalis, each 3 or 4 equivalents of it rendering 1 equivalent of either caustic soda or potash insoluble.

Properties of the Ferrocyanides.

Potassium ferrocyanide crystallises from aqueous solutions in large, well-formed, orange-yellow tetragonal pyramids of the composition $K_4Fe(CN)_6,3H_2O$; sp.gr. 1·86. The crystals do not change when exposed to the air at ordinary temperatures. They begin to lose water at 60°, and the finely powdered salt may be completely dehydrated at 100°, leaving a white powder which decomposes, in absence of oxygen, slightly below a red heat to a mixture of potassium cyanide, carbon and iron, nitrogen escaping. The powder takes fire at a considerably lower temperature when heated in contact with air. It is insoluble in alcohol. According to Etard (Ann. Chim. phys. 1894 [7] 2, 546), the solubility, expressed in grams of anhydrous salt dissolved by 100 grams of water, is 14·5 at 0°, 24·5 at 20°, 36 at 40°, 49·5 at 60°, 64 at 75°, 70 at 80°, 72 at 89°, 74 at 98°, and 88 at 157°. The salt is much less soluble in solutions of potassium salts. The specific gravity of the aqueous solutions is given below (Schiff, Annalen, 1860, 113, 199):—

Grs. $K_4Fe(CN)_6,3H_2O$ per 100 grs. of solution	1	5	10	15	20
Sp.gr. at 15°	1·0058	1·0295	1·0605	1·0932	1·1275

Sodium ferrocyanide crystallises in large lemon-yellow monoclinic prisms or rhombohehra of the composition $Na_4Fe(CN)_6,10H_2O$ (Conroy, J. Soc. Chem. Ind. 1898, 17, 103), which are permanent when exposed to the air at the ordinary temperature, but are completely dehydrated at a little above 100°. The behaviour of the dry salt, when heated, resembles that of the potassium compound. The solubility in water (Conroy, J. Soc. Chem. Ind. 1898, 17, 103): grams anhydrous salt dissolved by 100 grams of water, is at 20°, 17·9; at 30°, 23·5; at 40°, 29; at 50°, 35·5; at 60°, 42·5; at 70°, 51·5; at 80°, 59·2; at 90°, 61; and at 100°, 63.

Calcium ferrocyanide $Ca_2Fe(CN)_6,12H_2O$ is extremely soluble in water; highly concentrated solutions are very viscous and crystallise with difficulty, yielding small yellow triclinic crystals of sp.gr. 1·68, which effloresce when exposed to the air and lose 11½ molecules of water at 40°. H. G. Colman (Journ. of Gas Lighting, 1910, 583) finds that the whole of the water is removed by heating the salt in a current of air. The dry salt begins to decompose (in absence of oxygen) at 500° yielding calcium cyanamide thus

$$Ca_2Fe(CN)_6=2CaCN_2+Fe+N_2+4C$$

(unpublished experiments made by the writer).

Calcium potassium ferrocyanide $K_2CaFe(CN)_6$ is a white powder consisting of small quadratic prisms which becomes slightly cream-coloured on exposure to light. It contains no water of crystallisation and, at 15°-17°, 100 grams of water dissolve 0·41 gram of it (J. Campbell Brown, Chem. Soc. Trans. 1907, 91, 1826).

Calcium ammonium ferrocyanide

$$Ca(NH_4)_2Fe(CN)_6$$

is a white, minutely crystalline powder, which becomes coloured on exposure to light; it is anhydrous; 100 grams of water, at 15°-17° dissolve 0·258 gram of the salt (J. Campbell Brown, *ibid.* 1907, 91, 1826).

Hydroferrocyanic acid $H_4Fe(CN)_6$ is prepared by adding concentrated hydrochloric acid to a saturated solution of potassium ferrocyanide (both should be free from dissolved oxygen) and then enough ether to saturate the solution. The acid crystallises out in colourless scales which are washed with water saturated with ether (A. Joannis, Ann. Chim. Phys. 1882 [5] 26, 484), and dried over sulphuric acid. A solution of the acid, saturated at 14°, contains 150 grams per litre. The solution is readily oxidised by atmospheric oxygen, especially at higher temperatures, forming a blue substance which is usually assumed to be Prussian blue. This reaction is utilised in calico printing for the production of blue patterns.

Hydrogen ferrous ferrocyanide

$$H_2Fe[Fe(CN)_6]$$

is formed when a solution of the acid is boiled:

$$2H_4Fe(CN)_6=6HCN+H_2Fe[Fe(CN)_6].$$

Potassium ferrous ferrocyanide (Everitt's salt) $K_2Fe[Fe(CN)_6]$ is formed in a similar way if potassium salts are present, as, for example, in the preparation of hydrocyanic acid by distilling a mixture of potassium ferrocyanide and dilute sulphuric acid. Everitt's salt is a pale-yellow crystalline powder which is not identical with the white precipitate obtained by mixing solutions of potassium ferrocyanide and ferrous chloride, although this precipitate has the same composition.

Molecular constitution.—The soluble ferrocyanides all yield the complex ferrocyanogen ion, $Fe(CN)_6''''$; their aqueous solutions do not, therefore, exhibit the ordinary reactions of

ferrous or of cyanogen ions. The solutions are, however, not entirely devoid of these ions, we must rather consider them as being present in extremely small quantities in equilibrium with ferrocyanogen ion $Fe(CN)_6'''' \rightleftarrows Fe'' + 6CN'$. The increased quantity of silver nitrate required to produce opalescence in a solution of a cyanide when a ferrocyanide is added to it (Clennel, Chem. News, 1895, 72, 227; Conroy, J. Soc. Chem. Ind. 1896, 15, 12), is possibly due to this. The decomposition of ferrocyanides by mercuric salts is explained similarly, for the concentration of cyanogen ions which can exist in equilibrium with mercuric ion is even smaller than that in equilibrium with the ferrocyanogen ion. Hence the addition of mercuric ion to the solution removes cyanogen ion in the form of undissociated mercuric cyanide and so causes fresh quantities of the ferrocyanogen ion to dissociate. The dissociation of the ferrocyanogen ion is increased by exposure to light, so that in the light, alkaline sulphides produce a precipitate of ferrous sulphide and oxygen precipitates ferric hydroxide (from alkaline solutions), reactions which do not occur in the dark (Haber, Zeitsch. Elektrochem. 1905, 11, 846).

Very accurate measurements of the osmotic pressure and electrical conductivity of solutions of the ferrocyanides of calcium, strontium, and potassium have been made by the Earl of Berkeley, Hartley and others (*Phil. Trans.* 1909, 209 A, 177 and 319), which are best interpreted by assuming the salts to consist of double molecules which dissociate into 6 ions (or 10 in the case of the potassium salt). A complex structure of this kind would not be surprising in view of the great number and diversity of the ferrocyanides, especially those of iron.

Potassium ferricyanide, red prussiate of potash, $K_3Fe(CN)_6$ was discovered by Leopold Gmelin in 1822. He prepared it by passing chlorine into a solution of potassium ferrocyanide until it no longer gave a blue colour with a ferric salt:

$$2K_4Fe(CN)_6 + Cl_2 = 2K_3Fe(CN)_6 + 2KCl.$$

The salt is always manufactured by this reaction, the ferrocyanide is sometimes used in the form of a dry powder, in which case a mixture containing potassium chloride is obtained. Most commonly, a cold 10 p.c. solution of potassium ferrocyanide is treated with chlorine until conversion is just complete. A little Prussian green is always formed by the action of chlorine on the ferricyanide, and as this passes through any filter it spoils the appearance of the product. The difficulty may be avoided by evaporating the solution to crystallisation and then adding a little caustic potash which decomposes the green into ferric hydroxide, which is easily removed by filtration, and potassium ferrocyanide, which is apt to crystallise out along with the ferricyanide. The yield of ferricyanide, in this process, is 85 to 90 p.c. of the theoretical quantity.

A. W. Williamson (Annalen, 1846, 57, 225) found that potassium ferric ferrocyanide (Williamson's blue), when boiled with potassium ferrocyanide, gives potassium ferricyanide and Everitt's salt,

$$K_4Fe^{II}(CN)_6 + KFe^{III}[Fe^{II}(CN)_6] = K_2Fe^{III}(CN)_6 + K_2Fe^{II}[Fe^{II}(CN)_6].$$

Since Everitt's salt is readily oxidised to Williamson's blue by warming with dilute nitric acid, the process might (as Dittmar suggested) be utilised to complete the conversion of ferro- into ferricyanide, chlorine being used up to the point at which Prussian green begins to be formed.

Many other oxidising agents have been suggested in place of chlorine, such as bromine, lead peroxide, calcium plumbate, potassium permanganate and persulphate, and electrolytic oxidation (*see* Bertelsmann, Technologie der Cyanverbindungen).

Potassium ferricyanide crystallises from water in magnificent, deep-red, monoclinic prisms which may be very large. It is anhydrous; sp.gr. 1·845. The aqueous solution has an intense yellow colour. The solubility (grams of anhydrous salt dissolved by 100 grams of water) is 33 at 4·4°, 36 at 10°, 40·8 at 15·5°, 58·8 at 37·8°, 77·5 at 100°, and 82·6 at 104·4° (Wallace, Dingl. poly. J. 1856, 142, 52). Specific gravity of the solutions at 15° (Schiff, Annalen, 1860, 113, 199):—

Per cent. $K_3Fe(CN)_6$	1	5	10	15	20	25	30
Sp.gr.	1·0051	1·0261	1·0538	1·0831	1·1139	1·1462	1·1802

The aqueous solution is decomposed by light, potassium ferrocyanide being formed. The caustic alkaline solution is a strong oxidising agent which decolourises indigo instantaneously.

Prussian blue. The blue compounds of iron and cyanogen are all amorphous substances, some of which yield colloidal solutions in pure water. It is therefore extremely difficult to prepare them in a pure condition. Owing to the well-known tendency of colloids to absorb other substances from solutions, the precipitates require very prolonged washing to free them from adhering salts, and during this process their composition may, and very often does, change, owing to atmospheric oxidation or to hydrolysis. On the other hand, the method of determining the composition of a precipitate by mixing known quantities of the reagents and estimating the excess left in the supernatant liquid, is open, in this case, to the objection that the precipitate is not a pure substance because it has absorbed some of the salts in the solution in contact with it. The composition of the precipitates obtained by mixing the same substances depends, too, on the order of mixing and on the temperature and degree of acidity of the solutions, so that contradictory results have often been recorded by different observers. The whole subject has been reinvestigated recently by K. A. Hofmann (K. A. Hofmann, O. Heine, and F. Höchtlen, Annalen, 1904, 337, 1; K. A. Hofmann and F. Resensheck, *ibid.* 1905, 340, 267; 1905, 342, 364) and his co-workers, and the following account of the different 'blues' is based mainly on this work.

The freshly prepared blue precipitates contain indefinite quantities of water, but the whole of it cannot be removed by drying *in vacuo* over phosphorus pentoxide until a constant weight is attained (which usually requires from 2 to 5 months). This residual water must be regarded as constitutional, because when the substances are heated to temperatures a little above 100°, they lose cyanogen, but not water. The formulæ of the substances given in what follows refer to

the very thoroughly washed substances after complete drying over P_2O_5 in the way mentioned above.

When cold neutral solutions of one molecule of a ferric salt and one molecule of potassium ferrocyanide are mixed together, a precipitate of ordinary soluble Prussian blue is formed. The dry substance has the composition

$$2[KFe^{III}(Fe^{II}Cy_6)]+3\tfrac{1}{2}H_2O.$$

The same compound is obtained by mixing equal molecular quantities of a ferrous salt and potassium ferricyanide. This was first proved by Skraup (Annalen, 186, 371, 1877).

When a cold solution of potassium ferrocyanide is added gradually to a cold neutral (or ½ p.c. hydrochloric acid) solution containing an excess of a ferric or of a ferrous salt, or when soluble Prussian blue is digested with a solution of ferric chloride, precipitates are formed which, after the prolonged exposure to air involved in washing them completely, are identical in composition and properties. The dry substance is normal ferric ferrocyanide

$$Fe_4^{III}(Fe^{II}Cy_6)_3+10H_2O,$$

usually referred to as Prussian blue. Turnbull's blue, obtained by precipitating a solution of potassium ferricyanide with an excess of a ferrous salt, is identical with ordinary Prussian blue.

The precipitates obtained from hot acid solutions differ more or less from these in their properties, and appear to be mixtures of different substances.

Both the soluble and insoluble Prussian blue, just described, are ferric ferrocyanides, and not ferrous ferricyanides. This is proved by the fact that they can be made by the action of hydrogen peroxide on a solution containing a ferric salt and potassium ferricyanide in suitable quantities. As Schönbein (J. pr. Chem. 1866, 98, 65) showed, hydrogen peroxide reduces ferricyanide to ferrocyanide, but has no action on a ferric salt, so that ferrous ferricyanide could not be produced by this reaction.

Blue compounds, which are not identical with those described above, are also obtained by the oxidation of ferrous ferrocyanides.

(*a*) By adding a cold neutral solution of 1 molecule of a ferrous salt to a solution of 1 molecule of potassium ferrocyanide, and then oxidising the white precipitate by means of atmospheric oxygen, which is greedily absorbed (or better by hydrogen peroxide), a blue compound of the composition $KFe^{III}(Fe^{II}Cy_6)+H_2O$ is obtained. This differs from ordinary soluble blue in being insoluble in oxalic acid solution. It is referred to in the table of the properties of the blues as K. A. Hofmann's blue.

(*b*) By proceeding exactly as in (*a*), except that the solutions contain 1 p.c. of sulphuric acid, a white precipitate is obtained, $Fe^{II}K_2(Fe^{II}Cy_6)$, which is rather less readily oxidised to a blue of the same composition as before:

$$Fe^{III}K(Fe^{II}Cy_6)+H_2O,$$

but possessing rather different properties. Like ordinary soluble Prussian blue, it is soluble in water and oxalic acid, but it differs from it in being much more stable to ammonia solution. This compound is referred to as 'stable soluble blue.'

(*c*) When a solution of potassium ferrocyanide, containing about 10 p.c. of sulphuric acid, is heated in an atmosphere devoid of oxygen, one half of the hydrocyanic acid is evolved and a pale-yellow crystalline powder of Everitt's salt $K_2Fe^{II}(Fe^{II}Cy_6)$ remains behind. This salt is very much less readily oxidised than the precipitate obtained by mixing solutions of potassium ferrocyanide and a ferrous salt, it is not completely oxidised by several weeks' exposure to the air. As already mentioned, it is readily oxidised by warm dilute nitric acid, but a homogeneous product is prepared most certainly by suspending it in 1 p.c. sulphuric acid and adding about 10 times the theoretical quantity of hydrogen peroxide. The substance thus obtained is Williamson's blue (sometimes called violet), and it also has the composition $KFe^{III}(Fe^{II}Cy_6)+H_2O$. Its properties are, however, totally different from those of the isomeric substances already described.

For comparison, the distinguishing properties of the different blues are tabulated below. The isomerism of these substances may be due to differences in the linking of the atoms—of the kind familiar in organic chemistry—or it may be due to differences in the size of the molecules; the data available do not appear to be sufficient to decide these questions with any degree of certainty.

It is of interest that precipitation from hot acid solutions always tends to produce substances (or mixtures) of a more stable type, approaching Williamson's blue more or less closely in properties, and also that all the blue iron cyanogen compounds contain both ferrous and ferric iron. The compounds which contain only ferrous or only ferric iron are colourless or (compared with the blues) feebly coloured. Solid pieces of ordinary Prussian blue assume a coppery lustre when rubbed on a smooth, hard surface. The blue solution in oxalic acid was formerly used as an ink. Chlorine turns a suspension of Prussian blue in water green; the solution contains ferric chloride: the blue colour is restored by washing with water. Concentrated sulphuric acid unites with Prussian blue to a white paste from which the original blue is obtained by diluting with water. It is slowly decomposed by concentrated aqueous hydrochloric acid, but dissolves to a colourless solution in alcoholic hydrochloric acid; the solubility increases with the molecular weight of the alcohol used. Water precipitates unchanged Prussian blue from these solutions. Potassium, sodium, and calcium hydroxides decompose Prussian blue into ferric hydroxide and a ferrocyanide; alkali carbonates act more slowly. Tissues dyed with Prussian blue gradually lose their colour in sunlight, but regain it in the dark. When heated to about 170° in the air, it burns like tinder leaving a brown ash.

Commercial blues are usually mixtures of the compounds already described. J. G. Gentele (Lehrbuch der Farbenfabrikation, 2nd ed. 1880) says that the best blues are obtained by precipitating a ferrous salt with yellow prussiate and then oxidising the precipitate. *Paris blue* (the finest quality of commercial Prussian blue) is made as follows: 50 kilos. of yellow prussiate are dissolved in 250 kilos. of

PROPERTIES OF THE BLUE IRON-CYANOGEN COMPOUNDS.

Reagent	Ordinary soluble Prussian blue (Turnbull's soluble blue)	Insoluble Prussian blue (Turnbull's blue)	K. A. Hofmann's blue	Stable soluble blue	Williamson's blue or violet
Pure water	Soluble, reddish-blue solution	Insoluble	Soluble, green sh-blue solution	Soluble	Insoluble, turbid greenish-blue suspension
10 p.c. oxalic acid	Soluble, blue solution	Soluble, blue solution	Insoluble	Soluble	Insoluble
4 p.c. ammonia yields red-brown ferric hydroxide	In a few seconds	In 10 seconds	In a few seconds	In 6 to 7 minutes	After some hours
Ferric chloride	Precipitates insoluble Prussian blue	No change	(?)	Gradually coagulated in unchanged condition	No change
1 to 1½ p.c. H_2SO_4	Slowly precipitated, moist precipitate soluble in water	No action	Quickly precipitated; insoluble in water	Precipitated, insoluble in water	No action
Appearance of dry solids	Deep-blue with coppery lustre	Deep-blue purple lustre	—	—	Purple-red

boiling water; 42·5 to 45 kilos. of green vitriol are dissolved in about the same quantity of water, preferably in the presence of scrap iron to prevent formation of ferric salt. The clear solutions are then run simultaneously into 250 kilos. of water. The almost white precipitate is allowed to settle and then drained on a cloth filter. The oldest method of 'blueing' the paste was to heat it to boiling in a basin, transfer it to a wooden tub, and add 25·5 kilos. of nitric acid (sp.gr. 1·23) and 18 kilos. of sulphuric acid (1·84 sp.gr.). Sometimes, red fumes were evolved only after some hours, but in presence of excess of green vitriol, they were always evolved at once and this gave the best colour. After standing for 24 hours, the mixture was suspended in a large quantity of cold water and allowed to settle. The washing by decantation was continued until the blue was free from sulphuric acid. It was then collected on linen filters, pressed into thin cakes, and cut up into cubes which were dried in the air and finally at 30°-40°. The yield was 39 to 39·5 kilos. of finished blue.

Another method was to treat the heated paste of ferrous ferrocyanides with ferric chloride, instead of with nitric acid, until the solution contained ferric in addition to ferrous salts, but according to Gentele, the cheapest and best method is to acidify the paste slightly with hydrochloric acid and pass chlorine gas into it until the solution shows a distinct 'ferric' reaction with ferrocyanide.

From these descriptions it is clear that commercial Paris blue must contain, in addition to ordinary insoluble Prussian blue, one or more of the potassium ferric ferrocyanides. In the commercial pigments, Paris blue is diluted with starch, heavy spar, gypsum, or burned and finely ground kaolin. The white admixture, after having been ground very finely by itself, is added to the Paris blue paste, and along with it passed through a colour mill. Very low qualities of blue are faced by rotating the dry cubes in a cask with the fine dust of pure Paris blue.

Hydrocyanic acid. Prussic acid (Ger. *Blausäure*). HCN.

This substance was discovered by Scheele in 1782 (Chemical Essays, London, 1786; reprinted 1901). He observed that *Lixivium sanguinis* loses its power of forming Prussian blue when it is exposed to the air, and traced this effect to the atmospheric carbon dioxide. Other acids also produced it, and the blue-forming principle was found in the vapour given off. By distilling the *lixivium* with sulphuric acid, he obtained an aqueous solution of hydrocyanic acid. A more convenient method of preparation was to heat potassium ferrocyanide with dilute sulphuric acid. In doing this, he obtained a blue residue (oxidised Everitt's salt or Williamson's blue). Finally, he prepared mercuric cyanide by boiling Prussian blue with mercuric oxide; by treating this with iron and sulphuric acid, he decomposed it into mercury and hydrocyanic acid which he distilled off. In 1783, Scheele found that hydrocyanic acid is inflammable, its combustion yielding carbon dioxide. He also proved that it contains nitrogen by synthesising it from ammonia. Equal parts of charcoal and potassium carbonate were heated to redness, but not sufficiently to melt the potash, in a crucible and then some ammonium chloride stirred in (for 2 minutes only); the mass was then thrown into water and a solution obtained which gave 'a great quantity of Prussian blue,' whereas a similar experiment without the sal-ammoniac yielded none.

The exact quantitative composition of prussic acid was ascertained by Gay-Lussac (Annales de Chimie, 1815, 95, 156). He showed that it is similar in constitution to hydrochloric and hydriodic acids, except that the

hydrogen is united with a compound radicle, CN, which he called '*cyanogène*,' which plays the part of an element in so far as it passes through many transformations unchanged.

Hydrocyanic acid itself is formo-nitrile H—C≡N. Like the nitriles, it is hydrolysed rapidly by boiling alkalis and slowly by mineral acids, whereas the isomeric *iso*cyanides are unaffected by alkalis but violently decomposed by acids. Anhydrous liquid hydrocyanic acid, and also the nitriles, do not dissolve silver cyanide, whilst *iso*cyanides dissolve it very readily. *Iso*cyanides are changed when heated into the corresponding nitriles, but pure hydrocyanic acid, which undergoes no change at the ordinary temperature, is converted at 100°, or in the cold in presence of potassium cyanide, into a black amorphous mass which contains a termolecular polymeride, aminomalononitrile $NH_2CH(CN)_2$. The physical properties of hydrocyanic acid also resemble those of the nitriles, especially its high dielectric constant of 95.

The metallic cyanides, however, appear to have the *iso*cyanide structure, M—N=C (Wade, Chem. Soc. Trans. 1902, 1613; Gautier, Ann. Chim. Phys. [4] 17, 103, 1869; Nef. Annalen, 270, 329, 1892; 287, 325, 1895).

Hydrocyanic acid is found in many plants, usually in the form of a glucoside. Of these, amygdalin, found in bitter almonds, laurel leaves, &c., is the best known; it is a compound of benzaldehyde, hydrocyanic acid, and maltose. The great millet (*Sorghum vulgare*), which is cultivated in most tropical countries for food, also contains, in the immature plants, a glucoside, dhurrin, which is a compound of *p*-hydroxybenzaldehyde, hydrocyanic acid and dextrose (Dunstan and Henry, Proc. Roy. Soc., 1902, 70, 153). Several cases of cattle being poisoned by the green plant have been recorded (Leather, Agric. Journ. of India, 1, 220, 1906).

Preparation of hydrocyanic acid.—A 2 p.c. solution used in pharmacy is made by distilling a mixture of 2 parts of strong sulphuric acid diluted with 6 parts of water and 3 parts of yellow prussiate almost to dryness, and diluting the distillate to the strength required.

The most convenient method, however, is to run a solution of commercial sodium cyanide (97–98 p.c. NaCN) in about twice its weight of water into a small excess of cold 60 p.c. sulphuric acid. The hydrocyanic acid can be produced in this way at any desired rate; it is almost anhydrous, and the yield is practically quantitative. The sulphuric acid must not be added to the cyanide solution, because a part of the hydrocyanic acid produced in contact with the cyanide is polymerised and the solution becomes dark brown. The vapour may be dried by calcium chloride, kept at a temperature of about 30° and then condensed in a vessel cooled by ice, although the greater part of it is quite readily liquefied in an ordinary Liebig's condenser cooled by cold water.

Synthesis of hydrocyanic acid.—The earliest synthesis of hydrocyanic acid was effected by Clouet (Ann. de Chim. 1791, 11, 30), by passing dry ammonia over wood charcoal heated to bright redness in a porcelain tube. This reaction has been studied quantitatively by E. Bergmann (Journ. für Gasbel. 1896, 39, 117), D. Lance (Compt. rend. 1897, 124, 819), and G. A. Voerkelius (Dissertation, Hannover, 1909). The formation of hydrocyanic acid begins at about 700°, and the best yields, calculated on the ammonia used, are obtained at temperatures between 1000° and 1100°. The reaction $NH_3+C \rightleftarrows HCN+H_2$ is reversible, and should lead to an equilibrium between ammonia, hydrocyanic acid, and hydrogen; the equilibrium, however, cannot be realised, because both ammonia and hydrocyanic acid are unstable at the temperatures required. The final result depends, therefore, on the rates of decomposition of ammonia and hydrocyanic acid and on the rate of reaction between ammonia and charcoal. Even at 1000°, the rate of decomposition of hydrocyanic acid in presence of charcoal is small, but in presence of other substances it may be large. Voerkelius, for example, passed a mixture of hydrocyanic acid and hydrogen through an unglazed porcelain tube at 1000°, and found that over 70 p.c. of it was decomposed, but after a layer of carbon had been deposited on the tube the decomposition fell to 19 p.c. The rate of decomposition of the ammonia is even more variable; for example, at 720°, 28 p.c. of the ammonia survived 6 minutes' contact with fresh finely ground wood charcoal, whilst 82 p.c. were unchanged when the charcoal was in the form of lumps which had been already used. The rate of decomposition of the ammonia is diminished by diluting it with an indifferent gas.

In the 66 experiments recorded by Voerkelius, the ammonia (diluted with hydrogen) was in contact with the charcoal for from 16 to 360 seconds; within these limits, the ratio between the numbers of molecules of ammonia and of hydrocyanic acid in the product is roughly independent of the time of reaction, but the quantity of ammonia decomposed into its elements increases with the time of contact. The following table is calculated from the figures given by Voerkelius. The figures show the influence of the quality of the charcoal on the result:—

Temperature		P.c. NH_3 in gas used	Mols. NN_3 / Mols. HCN in product	
720°	charcoal A	50	6·7–13·4	mean 9·80
	„ B	50	29–45	„ 37·7
	sugar charcoal	50	71	„ 71
1020°	charcoal C	13–15	0·64–0·92	„ 0·76
	„ D	13–15	0·90–1·80	„ 1·40
	„ C	43–47	0·50–0·90	„ 0·61
1120°	„ D	13·4	0·44–0·48	„ 0·46

Nernst's thermodynamic theorem (Applications of Thermodynamics to Chemistry, London, 1907, and Theoretische Chemie, 5th and 6th ed.) has been applied to this reaction by v. Wartenberg (Zeitsch. anorg. Chem. 1907, 52, 299). Since the reaction $NH_3+C=HCN+H_2$ absorbs 39,500 cals. *per molecule*, the equilibrium must lead to the formation of more hydrocyanic acid at higher temperatures, the calculation indicates that the ratio of the partial pressures (in atmospheres) of the gases in equilibrium should have the following values:—

Temperature	$\frac{p_{NH_3}}{p_{HCN} \times p_{H_2}}$
500°	632
800°	0·27
1100°	0·003
1400°	0·0002

In the experiments tabulated above, the final mixture of gases usually contained nearly 95 p.c. of hydrogen, the partial pressure of which was therefore almost 1 atmosphere. The molecular ratio of ammonia to hydrocyanic acid is, therefore, almost the same as the ratio of the partial pressures. A comparison of the experimental values with those calculated shows that equilibrium is never even approximately attained, They agree in indicating 700° as the lowest temperature at which appreciable quantities of hydrocyanic acid can be formed.

This reaction has been discussed at some length, because there can be little doubt that the hydrocyanic acid in coal gas is formed by it.

That *nitrogen* and *acetylene* form hydrocyanic acid, $C_2H_2+N_2=2HCN$, was discovered by Berthelot (Compt. rend. 67, 1141, 1868). He passed strong sparks from an induction coil through a mixture of acetylene, nitrogen, and hydrogen, the latter being added to prevent the decomposition of acetylene, and found that hydrocyanic acid was formed. He also showed that the reaction is reversible, a mixture of hydrocyanic acid and hydrogen, when sparked, yielding acetylene and nitrogen. Since Berthelot had already discovered that acetylene is formed from carbon and hydrogen at the temperature of the electric arc, and also that hydrocarbons, in general, yield variable quantities of acetylene at high temperatures, it followed that hydrocyanic acid must be formed in the carbon arc in an atmosphere of hydrogen and nitrogen, and also when sparks are passed through mixtures of nitrogen and hydrocarbons.

Hutton and Smith (Eng. Pat. 23835, of 1906, and Trans. Amer. Electrochem. Soc. 13, 359, 1908) showed that the temperature of the arc is not necessary, hydrocyanic acid being formed when a carbon rod is heated in a mixture of hydrogen and nitrogen to 1700°; and H. v. Wartenberg (Zeitsch. anorg. Chem. 52, 299, 1907) carried out quantitative measurements with the following results (using a mixture of equal volumes of hydrogen and nitrogen):—

Temperature	P.c. HCN in the gas in equilibrium
1635°	1·95
1752°	3·10
1875°	4·70

Wallis (Annalen, 1906, 345, 353), by passing the same mixture through the electric arc at varying rates obtained a maximum of 33·5 p.c. of HCN in the gas. The estimated temperature of the arc is about 3250°.

Several modifications of this synthesis have been investigated, in which the carbon is derived from hydrocarbons or carbon monoxide and the nitrogen from ammonia, but none of them has attained any practical importance.

The *oxidation of organic compounds* by nitric acid often yields hydrocyanic acid in greater or smaller amount, and it has been proposed to manufacture hydrocyanic acid in this way. The interesting reaction described by Huntington (Eng. Pat. 14855, 1895) may be mentioned here. A mixture of acetylene and nitric oxide is readily exploded by a spark, yielding very considerable quantities of hydrocyanic acid in accordance with the equation

$$2NO+2C_2H_2=2HCN+2CO+H_2.$$

When *ammonium formate* is distilled, water is first given off together with a little ammonia and formic acid; at 180° formamide begins to distil over, and, as the temperature gradually rises to 220°, this is accompanied by increasing quantities of carbon monoxide, but only traces of hydrocyanic acid are produced. In order to obtain a good yield of hydrocyanic acid, the vapour must be heated to much higher temperatures, and the result is greatly influenced by the nature of the substance with which it is in contact. According to unpublished experiments by the writer, the principal changes which occur are:—

$$H\cdot COONH_4=HCO\cdot NH_2+H_2O \quad (1)$$
$$H\cdot COONH_4=NH_3+HCOOH$$
$$=NH_3+H_2O+CO \quad (2)$$
$$HCO\cdot NH_2=HCN+H_2O$$
$$H_2O+CO=CO_2+H_2.$$

The ammonia and hydrocyanic acid in the product usually accounted for more than 95 p.c. of the nitrogen in the ammonium formate or formamide used. Under similar conditions, the yield of hydrocyanic acid obtained from formamide is much greater than that obtained from ammonium formate. For each contact substance there is a certain temperature at which the yield is a maximum. The following table contains the best temperatures and corresponding yields for several contact substances:—

Contract substance	Ammonium formate		Formamide	
	Yield of HCN p.c. of theoretical	Temperature	Yield of HCN p.c. of theoretical	Temperature
Porcelain chips	41·5	700°	75	800°
Copper gauze	43·0	just below 500°	78	600°
Iron wire	39·0	just below 500°	—	—
Charcoal	21·0	420°	55	400°

With finely divided nickel, no hydrocyanic acid was obtained in any circumstances; at 273°, 92½ p.c. of the nitrogen was recovered as ammonia, but much less at higher temperatures.

Ammonia and carbon monoxide were said to yield hydrocyanic when passed over heated spongy platinum (Kuhlmann, Annalen, 38, 62, 1841), $CO+NH_3=HCN+H_2O$, and this apparently simple reaction has attracted several inventors. A careful investigation by Jackson and Laurie (Chem. Soc. Trans. 1905, 87, 433) has shown that a dry mixture of the two gases, when sparked, treated by the silent discharge or heated in presence of platinum (an electrically heated spiral of platinum wire gives the best result) yields ammonium cyanate thus:

$$CO+2NH_3=NH_4CNO+H_2,$$

and Kuhlmann's reaction does not take place.

The reverse change, $HCN+H_2O=CO+NH_3$, however, does occur very readily, even at 200°, when a mixture of steam and hydrocyanic acid is passed over broken brick as contact material, and at 600° it is practically quantitative. With iron oxide as contact substance, the conversion into ammonia is complete at 285°, and with Weldon mud at 200° (Carpenter and Linder, J. Soc. Chem. Ind. 24, 63, 1905).

Properties of hydrocyanic acid.—A colourless liquid possessing a characteristic smell (or rather taste), which produces a choking sensation in the larynx. It is one of the most poisonous substances known. Dogs are killed by a dose of about $\frac{1}{1500000}$ part of the weight of their blood: the fatal dose for a man is about 0·05 gram. The poisonous properties of the cyanides are probably due to the liberation of hydrocyanic acid by the acids of the stomach. The simplest and most effective antidote is prepared by mixing solutions of ferrous sulphate and sodium carbonate (suitable quantities are 50 c.c. each of solutions containing 150 grams of $FeSO_4,7H_2O$ and 57 grams of Na_2CO_3 per litre). Stimulants, such as ammonia, are also helpful. The writer has seen a dog, which had swallowed some potassium cyanide, and was already partially paralysed in its hind quarters, recover in a few seconds when dosed with the above mixture which had been made up hastily from ferrous ammonium sulphate. Subcutaneous injection of hydrogen peroxide, which converts hydrocyanic acid into oxamide, has also been recommended.

The sp.gr. of the liquid acid is 0·7058 at 7° and 0·6969 at 18° (Gay-Lussac). Freezing-point, −15° (Gay-Lussac), −13·4° (Tamman). The freezing-point is raised by pressure; it is −2·88° under 500 kilos. per sq. cm., and +50·1° under 4000 kilos. per sq. cm. pressure. The boiling-point under atmospheric pressure is 26·5°, and the vapour pressure is ½ atmo. at 4·5° (Gay-Lussac). The heat of evaporation is exceptionally large, 210·7 cals. per gram. The acid is miscible with water, ether, and alcohol in all proportions, almost insoluble in light petroleum. It is one of the weakest acids; its dissociation constant at 18°, $1·3\times10^{-9}$, is 44 times smaller than that of sulphuretted hydrogen, and 230 times smaller than that of carbonic acid (Walker and Cormack, Chem. Soc. Trans. 77, 16, 1900). In a 0·1*N*-solution, only 0·01 p.c. of the acid is dissociated into its ions, consequently it does not behave as an acid to indicators, and its salts are more or less completely decomposed by water; thus for example, $KCN+H_2O\gtrless KOH+HCN$. In 0·1*N*-solutions of the sodium or potassium salts, 1·1 p.c. is dissociated in this way; in *N*-solutions, only 0·3 p.c. at 24·2° (Shields, Zeitsch. physikal. Chem. 12, 167, 1893). This is of importance when it is required to concentrate an aqueous solution of a cyanide; the free hydrocyanic acid escapes until sufficient excess of the base has accumulated to reduce the hydrolysis to negligible proportions. In the case of weaker bases, the result is a considerable loss of hydrocyanic acid; with calcium cyanide, for example, the quantity of lime formed is greater than can be retained in solution, consequently equilibrium is never attained, and when such a solution is evaporated, the whole of the hydrocyanic acid escapes, leaving a residue of pure lime.

All the soluble cyanides are dissociated electrolytically in aqueous solution, except the mercury salt, which, as already mentioned, exists almost wholly in the form of undissociated molecules. Cyanogen ion has a great tendency to form complex anions by uniting with neutral molecules, the most important of these are $Ag(CN)_2'$, $Au(CN)_2'$, $Fe(CN)_6'''$ and $Fe(CN)_6''''$.

Cyanogen (Ger. *Cyan*) C_2N_2 was discovered by Gay-Lussac. It is prepared by heating perfectly dry mercuric cyanide at a dull red heat, $Hg(CN)_2=Hg+C_2N_2$. A part of the cyanogen is always polymerised to dark-brown, non-volatile paracyanogen. Cyanogen itself is a gas which burns with a peach-blossom-coloured flame. Liquid cyanogen boils at −20·7° under atmospheric pressure and freezes at −34·4°. Its heat of formation from graphite and nitrogen is—70,000 cals. per molecule. Water dissolves 4·95 times its volume of the gas at 0°. At 18° the dissolved cyanogen is hydrolysed to hydrocyanic and cyanic acids, the latter yielding ammonia and carbon dioxide so that no definite solubility is observed (Naumann, Zeitsch. Elektrochem. 16, 772, 1910). After some time the solution deposits dark brown azulmic acid and contains also oxalic acid and urea. Cyanogen dissolves in caustic alkalis, yielding cyanide and cyanate: $2KOH+C_2N_2=KCNO+KCN+H_2O$. Silver nitrate solution has no action on it; by means of these two reactions, it may be separated from hydrocyanic acid and estimated quantitatively in mixtures of the two gases (Wallis, Annalen, 345, 353, 1906). Cyanogen is very poisonous.

A knowledge of the exact conditions under which cyanogen can be formed from its elements is of interest in the theory of several technical processes for the manufacture of cyanides.

Wallis (Annalen, 345, 353, 1906) has shown that the electric arc burning between electrodes of very pure carbon in an atmosphere of nitrogen, produces no cyanogen at all. H. v. Wartenberg (Zeitsch. anorg. Chem. 52, 299, 1907) pointed out, however, that a very intense cyanogen spectrum is seen, and that carbon is deposited at some distance from the arc. Nernst's theorem indicates that very considerable quantities of cyanogen should exist in equilibrium with carbon and nitrogen at the temperature of the arc:

Temperature	Per cent. C_2N_2 in the gas calculated from Nernst's theorem
2000°	0·01
2500°	0·9
3000°	17·0
3250°	45·0

The probable explanation is that cyanogen is essentially unstable at low temperatures; that it can exist at all is due to an excessively slow rate of decomposition. Berthelot (Force des Matières Explosives, Paris, 1883, 113) has shown that it can be detonated by mercury fulminate, and, when heated, its rate of decomposition becomes measurable at 1200°. v. Wartenberg supposes, therefore, that cyanogen is really formed at the high temperature, but that it decomposes again completely before it can cool to temperatures at which it can continue to exist. It is obvious from the figures given above that the direct union of carbon and nitrogen to cyanogen can play no part in the formation of cyanides in processes which are carried out at ordinary furnace temperatures.

Potassium and sodium cyanides. The methods of manufacture of these salts are most conveniently described together, since most of the processes used may equally well be applied in making either salt. The most important technical processes have already been mentioned in the introduction to this article.

Manufacture from yellow prussiate.—Potassium cyanide was first prepared by Berzelius's method, which consists in heating dry potassium ferrocyanide to redness, when it decomposes thus: $K_4Fe(CN)_6 = 4KCN + Fe + 2C + N_2$. The loss of cyanogen, which occurs in this way, is partly avoided by fusing the ferrocyanide with potassium carbonate, as first described by F. and E. Rodgers (Phil. Mag. 1834, [3] 4, 91). Liebig showed that the product contains cyanate, formed thus:

$$K_4Fe(CN)_6 + K_2CO_3 = 5KCN + KCNO + Fe + CO_2$$

The fused salt is allowed to stand until the iron and carbon have settled out, and is then poured off into moulds. The comparatively small quantities of cyanide, which were used in electroplating and for other purposes up to about 1890, were made by this process. The product was sold in white, porcelain-like cakes, containing from 30 to 70 p.c. of KCN.

In 1876, E. Erlenmeyer (Ber. 1876, 9, 1840) pointed out that a very pure product, containing on the average 40 p.c. of CN (equivalent to 100 p.c. KCN), was obtained by fusing dry prussiate with metallic sodium in the proportions required by the equation

$$K_4Fe(CN)_6 + 2Na = 4KCN + 2NaCN + Fe.$$

This process was taken up first by the Deutsche Gold and Silber Scheide-Anstalt (F. Roessler, V. Inter. Kongress für Angewandte Chemie, Berlin, 1903, 1, 638) in Frankfort-on-Maine, in 1890; they obtained a practically quantitative yield by filtering off the spongy iron from the fused cyanide and pressing the iron while red hot. The cyanide so obtained is cast in cakes and forms a pure white crystalline mass. Since about 1905, sodium ferrocyanide has been used in this process in place of the potassium salt, and the product now made is almost pure sodium cyanide. The excess of the gas works cyanogen over that required in the colour industries is converted into sodium cyanide in this way.

The processes of Siepermann and Beilby were the first synthetic processes to produce cyanide in large quantities; they are most conveniently considered together because, although they differ widely in the methods adopted in carrying them out, they are both based on the same chemical reaction which, curiously enough, was also used by Scheele in the first synthesis of a cyanide which was ever made.

In Siepermann's process (D. R. P. 38012, March 10, 1886; Eng. Pat. 13697 of 1889; 9350 and 9351 of 1900) a dry mixture of about 2 parts of charcoal and 1 part of potassium carbonate—that is, a sufficient excess of charcoal to keep the mixture in the form of a dry unfused mass throughout the process—is heated in the upper part of a vertical iron tube to a dark-red heat and treated with dry ammonia gas, which is taken up, forming potassium cyanate. The product is then allowed to fall into the lower end of the tube, which is heated to bright redness. At the higher temperature the cyanate is converted into cyanide, the carbon monoxide evolved escaping through the upper part of the tube along with the hydrogen formed from the ammonia, without taking any part in the reaction. The finished material is drawn off into air-tight receptacles where it is allowed to cool completely, after which it is systematically lixiviated with water. Potassium cyanide may be precipitated from the solution obtained (sp.gr. about 1·4) by adding excess of potassium carbonate, but according to the later patents it is preferable to evaporate it almost to dryness and extract the unchanged potassium carbonate with small quantities of water at 66°. The residue of potassium cyanide and cyanate is then treated with water between −18° and +5°, which dissolves the cyanide and any residue of carbonate, leaving almost pure potassium cyanate. The product of this process was first put on the market in 1892 (G. Beilby, V. Int. Kongress angew. Chem. Berlin, 1903, 1, 630), but as the substance was in the form of a damp deliquescent mass, it could not be exported for use at the mines by itself but had to be fused with the product of the ferrocyanide process.

In the Beilby process (Eng. Pat. 4820, of 1891), which began to produce in the same year, the quantity of charcoal used is very much smaller, very little more being employed than is necessary to convert the potassium carbonate into cyanide thus:

$$K_2CO_3 + 4C + 2NH_3 = 2KCN + 3CO + 3H_2.$$

The charcoal is added gradually during the progress of the operation, so that the material is always in the form of a fused liquid through which the ammonia gas is forced under some pressure. This is continued until a sample shows the conversion to be sufficiently complete; it is then only necessary to separate the small excess of charcoal by filtration in order to have a pure white saleable product. Since the melting-point of pure potassium carbonate (890°) is inconveniently high, previously made cyanide was mixed with it in starting the process, or the more readily fusible mixture of sodium and potassium carbonates was used, so that the cyanide made by the process was very similar in composition to that produced by the Erlenmeyer process from potassium ferrocyanide.

It is difficult to obtain a satisfactory yield on the ammonia in these processes, owing to the rapidity with which it decomposes into its elements at temperatures above 500° and in contact with metals, especially iron (Ramsay and Young, Chem. Soc. Trans. 1884, 88; Beilby and Henderson, *ibid.* 1901, 1245). For this reason it is necessary to work at the lowest possible temperature. Siepermann, for example, obtained a yield of 86 p.c. on the ammonia when it was absorbed at a dark-red heat, but only 58 p.c. at a bright cherry-red heat. Readman (J. Soc. Chem. Ind. 8, 757, 1889) showed that almost theoretical efficiencies can be obtained at the low temperatures attainable in an ordinary organic combustion furnace; whilst Conroy (*ibid.* 15, 12, 1896), working at very high temperatures (1000°–1200°), could not get more than 30 to 33 p.c. of the ammonia in the form of cyanide.

The chemistry of the reaction has been investigated by J. Pfleger (F. Roessler, V. Int.

Kongress angew. Chem. Berlin, 1903, 1, 638). Ammonia and potassium carbonate react, yielding potassium cyanate and hydroxide, a carbamate being most probably formed as an intermediate product;

$$CO(OK)_2+NH_3=CO<\begin{matrix}NH_2\\OK\end{matrix}+KOH$$

$$CO<\begin{matrix}NH_2\\OK\end{matrix}=KCNO+H_2O.$$

When pure potassium cyanate is heated at 800°–900°, it decomposes, cyanide and carbonate being formed and nitrogen, carbon dioxide, and carbon monoxide evolved. The mechanism of this change is probably as follows; Drechsel has observed that the cyanates of the alkaline earth metals decompose, when heated, into carbon dioxide and the corresponding cyanamide salts. Assuming that the alkali cyanates behave similarly, the first change will be

$$2KCNO=K_2CN_2+CO_2.$$

Potassium cyanamide, however, decomposes completely at lower temperatures than 800° into cyanide, potassium, and nitrogen;

$$K_2CN_2=KCN+K+N.$$

The carbonate and carbon monoxide observed are thus due to the reaction between the metallic potassium and carbon dioxide which are formed simultaneously. In presence of charcoal in excess, the greater part of the cyanamide follows Drechsel's reaction (J. pr. Chem. 1880 [2] 21, 77), $K_2CN_2+C=2KCN$ instead of decomposing; so that the apparent reduction of cyanate by carbon probably takes place in the two stages:

$$2KCNO=K_2CN_2+CO_2$$

and $K_2CN_2+C=2KCN$

$$CO_2+C=2CO.$$

The reactions occurring in the Beilby process are the same, except that, the whole process being carried on at the higher temperature, the formation of cyanate and its conversion into cyanide take place simultaneously instead of being more or less sharply separated as they are in Siepermann's process.

In the Siepermann process, it is easier to use the ammonia efficiently, owing to the lower temperature employed, but this is counterbalanced by the greater difficulty of working up the product into a marketable form.

The Castner process.—In 1894 H. Y. Castner (Eng. Pat. 12219, of 1894) patented a process in which sodium was fed in at the upper end of a column of red-hot charcoal through which a current of dry ammonia gas was passed from below, the reaction being expressed by the simple equation:

$$2Na+2C+2NH_3=2NaCN+3H_2.$$

In a second patent (H. Y. Castner, Eng. Pat 21732, 1894) it is shown that better results are obtained by first allowing the sodium and ammonia to react at a low temperature (300° to 400°), forming sodium amide $NaNH_2$, and then running the amide on to an excess of red-hot charcoal with which it reacts thus:

$$NaNH_2+C=NaCN+H_2.$$

Working in this way, it happened on one occasion that an excess of amide was accidentally run into the vessel containing the charcoal, and a product of unusual appearance was obtained, in which the writer found a large quantity of sodium cyanamide. The reaction, therefore, takes place in three stages, in which the nitrogen enters successively into more and more stable combinations. First sodium amide is produced, a compound which begins to decompose rapidly into its elements at 500° (Titherley, Chem. Soc. Trans. 1894, 504); this reacts either with carbon

$$2NaNH_2+C=Na_2CN_2+2H_2,$$

or, as Pfleger found, with sodium cyanide

$$NaNH_2+NaCN=Na_2CN_2+H_2,$$

forming sodium cyanamide, a compound which only decomposes slowly at 600°, and finally this takes up carbon, forming sodium cyanide which is quite stable at any temperature attained in the process.

Like the Beilby process, this process yields a fused product containing very small quantities of solid impurities which are easily removed by filtration. After being cast in iron moulds, the cyanide is obtained in the form of pure white cakes with crystalline fracture, containing 97½ to 98 p.c. of NaCN (equivalent to 129–130 p.c. of KCN).

'Schlempe' process.—The juice of the sugar beet contains both inorganic and organic substances other than sugar, and these substances accumulate in the molasses. In Germany, rather more than half of the molasses made are treated with strontia, which combines with the sugar to an insoluble sucrate; the residue left after removing this, the concentrated essence of the impurities of the original juice, is known as 'schlempe.' After concentration to sp.gr. 1·4, it contains 75 p.c. of dry substances, 30 p.c. of which are inorganic (mainly potassium) salts and the remainder organic substances. The 'schlempe' contains about 4 p.c. of nitrogen in the form of betaïne

$$(OH\cdot N(CH_3)_3\cdot CH_2COOH)$$

and decomposition products of the vegetable proteïns. Of the molasses not treated by the strontia process, a large part is consumed as cattle food and a small part fermented to alcohol.

The first attempt to utilise the nitrogen of 'schlempe' was made by Vincent in 1877–1880. He distilled the 'schlempe' in horizontal iron retorts at a red heat, ammonia, a mixture of methylamines, methyl alcohol, and combustible gases were evolved, and potassium carbonate mixed with some carbon remained behind (H. Ost, Zeitsch. angew. Chem. 19, 609, 1906). In 1879 Ortlieb and Müller devised a process for converting Vincent's methylamines into hydrocyanic acid, which was worked by the Société Anonyme de Croix (Eng. Pat. 3844, of 1879). The vapour of the methylamines was passed through a red-hot retort, yielding ammonia, hydrocyanic acid, methane and hydrogen. The ammonia was absorbed by sulphuric acid, and the hydrocyanic acid by a suspension of ferrous hydroxide in caustic potash. The manufacture of the methylamines was abandoned in 1881 for want of a market, and with it the production of cyanides.

The problem was again attacked by Bueb (Reichardt and Bueb, Eng. Pat. 7171, of 1895; Bueb, Eng. Pat. 26259, of 1898). Instead of separating the products of distillation of the 'schlempe,' he passed them directly, after condensing some tar, into a series of firebrick

channels which were heated to bright redness. The ammonia and hydrocyanic acid were absorbed together in a solution of ferrous sulphate, and the product worked up in the way described on p. 185. The narrow flues were soon stopped up by deposits of carbon, so that they were replaced by chambers filled with fire-brick checker-work, which is heated up to 1000° by firing directly with producer gas; during this process, the deposit of carbon is burned. Two such chambers are used alternately, the one being heated up whilst the gases from the retorts are passing through the other. The gases leaving the decomposing chambers contain 7 p.c. HCN; 7 p.c. NH_3; 8 p.c. (mainly) CH_4; 12 p.c. H_2; 18 p.c. CO; 24 p.c. CO_2, and 24 p.c. N_2. In passing through the decomposing chamber, the methylamines disappear and hydrocyanic acid is formed, the ammonia undergoing but little change. The ammonia is now removed from the gas by absorption in sulphuric acid, and the hydrocyanic acid absorbed in caustic soda, but the exact method employed to separate it from the large quantity of carbon dioxide which accompanies it has never been published. The solution of sodium cyanide is evaporated to crystallisation, the crystals dried, and briquetted by compressing them into blocks which are dried at 70° *in vacuo* (Eng. Pat. 18096, of 1907), and then contain sodium cyanide equivalent to 120 p.c. of KCN.

Of the nitrogen in the 'schlempe,' about one-half is converted into nitrogen gas and so lost; a quarter is obtained as sodium cyanide and the remainder as ammonium sulphate.

The decomposition of di- and tri-methylamine, when passed through a heated porcelain tube filled with fragments of porcelain, fire-brick, or charcoal, has been studied by Voerkelius (Dissertation, Hannover, 1909). At temperatures lying between 800° and 1000°, as much as 98 p.c. of the trimethylamine decomposes into hydrocyanic acid and methane $N(CH_3)_3=HCN+2CH_4$, the remaining 2 p.c. yielding ammonia $N(CH_3)_3+3H_2=NH_3+3CH_4$. This result was obtained when the gaseous contents of the tube were changed once in 7½ seconds; with a slower current of gas and also with a contact material of large surface (fireclay or charcoal) or with iron, a part of the hydrocyanic acid is decomposed into its elements. The rate of decomposition at 1000°, however, is small. At 720° the yield of hydrocyanic acid was only 78 p.c., and at 600° none was produced.

The formation of hydrocyanic acid from dimethylamime also begins between 600° and 700°, from 800° to 1100° the change takes place quantitatively in accordance with the equation $NH(CH_3)_2=HCN+CH_4+H_2$. If hydrogen is present, however, a second change occurs, $NH(CH_3)_2+2H_2=NH_3+2CH_4$. Using equal volumes of hydrogen and dimethylamine, this reaction is of no importance, but as the hydrogen present increases more and more of the dimethylamine is converted into ammonia until, with a mixture of 97 parts of hydrogen to 3 parts of dimethylamine, ammonia is the sole product.

The behaviour of monomethylamine is probably analogous to that of dimethylamine. Wurtz found that considerable quantities of ammonia are formed by its decomposition.

In practice, therefore, the losses of hydrocyanic acid and ammonia by decomposition will depend on the rate of passage of the gases and on the nature of the contact material—the deposit of carbon on the porous bricks diminishing the decomposition of hydrocyanic acid.

Cyanides direct from sulphocyanides. Several processes for the direct conversion of sulphocyanides into cyanides, without passing through ferrocyanide, have been carried out on a manufacturing scale, although they have not been able to take a leading place in the production of cyanide.

The earliest of these was D. J. Playfair's process (Eng. Pat. 7764 of 1890). Playfair found that certain metals, lead and zinc especially, when fused with potassium sulphocyanide, abstract the sulphur, leaving potassium cyanide, which may be separated from the metallic sulphide by extraction with water. The fusion is carried out at 400°, and 70–80 p.c. of the sulphocyanide is converted into cyanide (D. J. Playfair, J. Soc. Chem. Ind. 11, 14, 1892; Conroy, *ibid.* 15, 8, 1896). The reaction is slower with lead, owing to the small surface offered by the fused metal, whilst with zinc the product is apt to be contaminated by the double cyanide of zinc and potassium. The process was worked about 1894 by the British Cyanides Co. at Oldbury (Brussels Exhib. 1910, Catalogue of British Chem. Section, p. 63).

Raschen's process (Eng. Pats. 10476, 10956 and 21678 of 1895; 19767 of 1898; 12180 of 1900) is based on the oxidation of sulphocyanic acid to hydrocyanic and sulphuric acids which was first observed by E. A. Hadow (Annalen, 1858, 108, 380). Hadow found that permanganate, lead peroxide, manganese dioxide, and nitric acid bring about the same reaction. Raschen found that it takes place quantitatively in acid solutions only when an excess of the oxidising agent is present. If the oxidising agent is added to the sulphocyanide, solid yellow compounds are produced of variable composition, one of which, 'canarin' (*q.v.*), has been used as a yellow dye.

The Raschen process (J. T. Conroy, J. Soc. Chem. Ind. 1899, 18, 432) was carried out by allowing a solution containing about 15 p.c. of sodium sulphocyanide to flow into dilute nitric acid kept at the boiling-point by means of live steam. The reaction:

$$NaCNS+2HNO_3=HCN+NaHSO_4+2NO$$

took place. From 3 to 5 p.c. of the nitric acid was less completely reduced, N_2O_3 being formed, so that the gases leaving the decomposer were first scrubbed with a little water. The resulting solution of nitric, nitrous, and hydrocyanic acids was returned to the decomposer. The gas, which now contained about 1 volume of hydrocyanic acid to 2 volumes of nitric oxide, was passed through a solution of caustic soda (sp.gr. 1·37), which absorbed the hydrocyanic acid. It was found necessary to avoid saturating this solution completely with hydrocyanic acid because of the brown decomposition products which are formed from the free acid in presence of a cyanide. The nitric oxide was then mixed with air and passed upwards through towers packed with flints down which water trickled; in this way it was reconverted into nitric acid (sp.gr. 1·12) which was returned to the decomposer. The solution of

sodium cyanide was evaporated to dryness in vacuum pans without appreciable loss.

The reduction of sulphocyanides by hydrogen was studied by Playfair (J. Soc. Chem. Ind. 11, 14, 1892). He found that hydrogen acts on potassium sulphocyanide at a dull-red heat, forming potassium cyanide and sulphide and sulphuretted hydrogen.

Conroy, Heslop, and Shores (J. Soc. Chem. Ind. 1901, 20, 320) showed that the reaction takes place slowly at 500°, and fairly fast at 600°. Their results indicate that two reactions occur simultaneously:

$$KSCN+H_2=KCN+H_2S$$

and

$$2KSCN+2H_2=K_2S+2HCN+H_2S.$$

A little ammonia is also evolved, probably owing to the difficulty of drying the sulphocyanide completely. About 70 p.c. of the nitrogen is obtained in the form of cyanide and 20 p.c. as hydrocyanic acid. With barium and cuprous sulphocyanides, the reaction is similar to that represented by the second of the above equations, the principal nitrogenous product being hydrocyanic acid. With the cuprous salt, the reaction begins below 300°.

Rossiter, Crowther, and Albright (Eng. Pat. 4403 and 6226, of 1901) have patented a process based on the behaviour of the cuprous salt. It is mixed with finely divided copper and heated at temperatures rising from 150° to 650° in a current of hydrogen. Hydrocyanic acid is evolved and cuprous sulphide remains behind.

Production of cyanides from atmospheric nitrogen. In every process at present used for the manufacture of cyanides, the nitrogen is derived from coal more or less directly. The production of cyanides from atmospheric nitrogen is a problem on which both money and chemical and engineering skill have been lavished without leading to any financially successful solution. An account of the cyanide industry would be incomplete without some description of these very interesting and instructive experiments.

The formation of potassium cyanide by the action of nitrogen on carbon and potassium carbonate, was observed by Desfosses (Ann. Chim. Phys. 1828, 38, 158), but the quantities formed either in laboratory experiments or in the blast furnace were so small compared with the quantities of materials used, that even as late as 1842 the source of the nitrogen in the cyanide was doubtful, some chemists holding that it was derived from the coal or charcoal employed. The first industrial application of the reaction was made by Possoz and Boissière (Eng. Pat. 9985, of 1843). Their process was worked by the inventors at Grenelle in France, in 1843, and from 1844 to 1847 at the works of Bramwell & Co. in Newcastle-on-Tyne. An account of these very interesting experiments was given by F. R. Hughes (Graham, Reports of Juries, Exhib. of 1851, I, 95), who was concerned in carrying them out.

Wood charcoal was soaked in a solution of ordinary potash and dried; this yielded a mixture containing about 20 p.c. of K_2O. This was at first heated in vertical fireclay retorts of small diameter, which were fired externally. Owing to the bad conductivity of the retort and of the charcoal, the heat penetrated the mass very slowly, and the output of a tube was very small. After a number of alterations, retorts were adopted which were built of ordinary firebricks: they were 2 feet in internal diameter, and were heated to a temperature sufficient to produce cyanide for a length of 6 to 8 feet. In an upper prolongation, the wet charcoal was dried and preheated, and in a lower, unheated extension, made of cast iron, the product was cooled down and then discharged, by means of an arrangement which permitted a periodical withdrawal of a part of the charge, into a solution of a ferrous salt, into which the lower end of the cast-iron tube dipped. A ring of small slots was left in the brick retort at every third or fourth course of bricks, through which the hot mixture of nitrogen and carbon dioxide in the furnace was drawn into the retort. In this way the difficulty of heating the mass to its centre was overcome. The highest temperature in the furnace was sufficient to soften a Stourbridge fireclay brick throughout its substance. The hot gases passed upwards through the retort, drying and preheating the fresh charge in its upper part. As much as one-half of the alkali in the cyanised charcoal produced was found to be in the form of cyanide, and 7 or 8 retorts of the dimensions given yielded 36 to 40 cwts. of prussiate of potash per week, under favourable circumstances. About one-half of the charcoal used was consumed, and three parts of potash were used for one part of prussiate made. About one-third of the potash was accounted for by the prussiate; one-third remained in the refuse charcoal, which could not be profitably lixiviated; and the remainder combined with the bricks of the retort or volatilised up the chimney. The financial failure of the process was due to the losses of potash and to the short life of the retorts.

Hughes suggested that potassium carbide may be the first product, and that the cyanide may be produced by its combination with nitrogen, an explanation of the process which was also given by Berthelot 17 years later. Although this process has attracted many subsequent inventors, no success has attended their efforts. The difficulties due to the high temperature required appear to be insuperable. Bunsen and Lyon Playfair (British Assoc. Reports, 1845, 185) showed, in 1845, that cyanide is only formed at temperatures sufficient for the production of metallic potassium. A few temperature measurements which the writer made with a platinum-rhodium thermocouple showed that potassium vapour is first evolved from a mixture of charcoal and potassium carbonate at about 1350°, and that the formation of cyanide takes place very slowly at this temperature, the potassium cyanide volatilising for the most part.

In 1860 Margueritte and De Sourdeval (Eng. Pat. 1171, of 1860) discovered that a mixture of barium oxide and carbon absorbs nitrogen at a much lower temperature than that required when potash is used. Ludwig Mond (Eng. Pat. 433, of 1882; J. Soc. Chem. Ind. 1889, 8, 505) experimented with this process in 1882. He found that a temperature of 1200° was required for the formation of cyanide, and that the reaction goes best about 1400°. The barium compounds fuse readily at these temperatures

and attack the fireclay retorts. To avoid this he briquetted them with an excess of carbon and pitch. The apparatus used was similar to that of Possoz and Boissière, and 40 p.c. of the barium used was readily cyanised. The object of Mond's experiments was the production of ammonia, and he abandoned this process in favour of the more promising method of acting on coal with air and steam in large excess (*see* AMMONIA).

In 1894 J. B. Readman (Eng. Pat. 6621, 1894) made a very considerable step in advance by introducing electrical heating. His process was worked by the Scottish Cyanides Co. at Leven in Fifeshire, between the years 1899 and 1907. Considerable quantities of sodium cyanide of excellent quality were produced, but the financial results were unfavourable. The following account of the process in its final form is believed to be substantially accurate.

Barium carbonate, produced in a later stage of the process, was intimately mixed with ground coal to a thick paste, which was dried and coked in ordinary gas retorts. The granular mixture of barium oxide and coke so produced was then fed into an electric furnace, consisting of a vertical shaft of magnesia bricks. A ring of carbon blocks in the wall of the shaft near its lower end formed one electrode, a carbon cylinder suspended in the mouth of the shaft formed the other. The alternating current passed between these electrodes through the granular mass of coke and barium oxide, heating it to a high temperature. A current of producer gas with about 70 p.c. of nitrogen, passed upwards through the mass, which was constantly fed downwards into a cooling chamber by means of a plate and rotating arm which closed the lower end of the shaft. The cooled product was lixiviated with water, and the resulting solution, containing barium cyanide and hydroxide, treated with sodium bicarbonate. After filtering off the barium carbonate, the solution of sodium cyanide was concentrated *in vacuo* and then passed over cooling coils depositing crystals of the hydrate $NaCN,2H_2O$. These were separated from the mother liquor in a centrifugal machine, and then dehydrated by heat and the powder briquetted.

The chemistry of this process is far from simple. Barium carbonate itself (as Finkelstein (Ber. 1906, 39, 1585) has shown) does not melt at 1350°, but when heated alone or with carbon, it is partially converted into barium oxide, which yields readily fusible mixtures with the carbonate. Le Chatelier found, for example, that partially decomposed barium carbonate melts at 795°. The fusibility of the mixtures is increased by the formation of barium cyanide (which melts about 600°), so that in practice the material undergoing treatment is a liquid mixture of the oxide, carbonate, and cyanide of barium absorbed in carbon. Nitrogen begins (Kühling and Berkhold, Ber. 41, 28, 1908) to react with barium oxide and carbon at 925°, but the reaction is reversible (writer's unpublished experiments), and may be expressed by the equation $BaO+3C+N_2 \gtrless Ba(CN)_2+CO$. The pressure of carbon monoxide required to decompose barium cyanide diminishes rapidly as the concentration of the latter increases, reaching extremely small values at temperatures below 1200°, when some 40 p.c. of the barium has combined with nitrogen. For this reason, a moderately complete conversion of the barium oxide into cyanide can only be effected at low temperatures by using an enormous excess of pure nitrogen, which is fatal to the economy of the process. This difficulty is avoided by resorting to higher temperatures (1400° to 1500°), at which the fixation of nitrogen will proceed in presence of considerable quantities of carbon monoxide, so permitting the use of producer gas in place of pure nitrogen. Unfortunately, however, a large part of the nitrogen fixed at the higher temperatures is in the form of barium cyanamide, which, when treated with water, yields barium hydroxide and free cyanamide.

While Readman's process was being worked out, the problem was attacked in a different way by Frank and Caro (Eng. Pat. 15066, of 1895) and by T. L. Willson (Eng. Pat. 21997, of 1895), who discovered independently, in 1895, that the carbides of the alkaline earths combine with nitrogen. Frank and Caro at first attempted to apply their discovery to the manufacture of cyanides.

Finely ground barium carbide, made in the electric furnace, was heated at about 700° in presence of pure nitrogen. The product contained about 11 p.c. of nitrogen, 30 p.c. of which was in the form of barium cyanide, the remainder being barium cyanamide. In order to convert the cyanamide into cyanide, the material was heated with dry sodium carbonate and carbon. The sodium carbonate probably converts the barium cyanamide into the sodium salt, which then takes up carbon in the way discovered by Dreschel,

$$BaCN_2+Na_2CO_3=Na_2CN_2+BaCO_3$$
$$\text{and } Na_2CN_2+C=2NaCN.$$

By extracting the product with water, converting the sodium cyanide into ferrocyanide, and then fusing it with sodium, about 86 p.c. of the nitrogen fixed was obtained in the form of marketable sodium cyanide (G. Erlwein, V. Int. Kongress angew. Chem. Berlin, 1903, 1, 646). The process, however, even in this form, did not pay, and the cheaper calcium carbide was therefore tried. Commercial calcium carbide absorbs nitrogen at about 1100°, yielding a product containing from 20 to 23·5 p.c. of nitrogen, which is wholly in the form of calcium cyanamide (Frank and Caro, Eng. Pat. 25476, of 1898), $CaC_2+N_2=CaCN_2+C$. By heating this product with sodium chloride, from 90 to 95 p.c. of the cyanamide is converted into sodium cyanide. The hydrocyanic acid may be set free by means of an acid, and then absorbed in caustic soda solution (G. Erlwein, V. Int. Kongress angew. Chem. Berlin, 1903, 1, 646).

Cyanides from nitrides. At high temperatures, nitrogen combines directly with several elements to form nitrides, and these, when fused with sodium carbonate and carbon, produce sodium cyanide. This has been shown to be the case with the nitrides of boron, calcium, magnesium, titanium, silicon, and aluminium, and with phospham PNH_2. Since none of these processes has emerged as yet from the experimental stage, it is sufficient to mention the possibility of producing cyanides in this way.

The Principal Cyanides.

Potassium cyanide KCN crystallises in anhydrous, colourless octahedra from aqueous solutions, or in cubes when the fused salt solidifies; sp.gr. 1·52. It melts at a dull-red heat, and volatilises without decomposition at high temperatures. It is readily soluble in water; the saturated solution contains 122·2 grams of KCN to 100 grams of water at its boiling-point (103·3°). At 19·5°, 100 grams of absolute alcohol dissolve 0·88 gram (Landolt, Börnstein and Meyerhoffer, Tabellen, Berlin, 1905). It deliquesces in moist air.

Sodium cyanide NaCN crystallises from the fused liquid in apparently cubic crystals; from aqueous solutions below 35° large colourless plates of the hydrate $NaCN,2H_2O$ are deposited. Joannis (Ann. Chim. Phys. 1882, [5] 26, 484) obtained a hydrate $NaCN,\frac{1}{2}H_2O$ from cold 85 p.c. alcohol. F. Roessler (Eng. Pat. 279, 1899) showed that the hydrate $NaCN,2H_2O$ decomposes at 33° (34·7° according to the writer's measurements) into the anhydrous salt and a saturated solution, about 40 p.c. of the sodium cyanide separating in the anhydrous state. The solubility of the hydrate (in grams of NaCN to 100 grams of water) is, 35·4 at −20°; 43·4 at 0°; 58·3 at 20° and 82 at 34°·7. The solubility of the anhydrous salt is almost independent of the temperature (82 grams per 100 grams of water). The sp.gr. of aqueous solutions of sodium cyanide at 25° is given by the expression $1+0·00534p$, where p is the percentage of NaCN. Sodium cyanide (96 p.c.) melts at 540°. The pure salt, when heated in a glass tube so as to be out of contact with metals, in a current of dry air free from carbon dioxide, remains entirely unchanged at temperatures up to 370°; if, however, it is in contact with iron or nickel, or if traces of the oxides of these metals are added to it, oxidation proceeds rapidly, cyanate and carbonate being formed and carbon dioxide evolved. The carbonate is formed by the oxidation of the cyanate, which is the primary product. Sodium cyanate behaves towards oxygen in exactly the same way as the cyanide; it is quite unaffected by dry air (free from CO_2) even at 400°, but when mixed with 1 p.c. of nickel oxide it oxidises rapidly; thus:

$$2NaCNO+3O=Na_2CO_3+CO_2+N_2$$

(writer's unpublished experiments).

Sodium cyanide absorbs moisture with great avidity from ordinary moist air. The writer has found that it takes up water from purified air saturated with aqueous vapour at 20° at all temperatures below 44°, but not at higher temperatures. This is of importance in sampling and analysing the salt.

Dilute solutions of potassium or sodium cyanide decompose very slowly in contact with the atmosphere, the loss being almost wholly due to absorption of carbon dioxide.

Liebig's statement that metallic iron is dissolved by solutions of potassium or sodium cyanide with evolution of hydrogen is true of the finely divided metal, but iron vessels may be used for years for boiling concentrated solutions of cyanides without requiring repair, and iron tanks are regularly used in the treatment of gold ores with cyanide solutions.

With the exceptions of lead and platinum, all ordinary metals are dissolved by cyanide solutions in presence of oxygen.

Zinc is slowly dissolved without oxygen, but if a piece of zinc is half immersed in a cyanide solution, it is eaten through at the surface of the liquid before any appreciable action has taken place on the submerged portion.

Alkali cyanides yield ammonia and a formate when boiled with water or treated with strong sulphuric acid, in the latter case the formic acid produced is at once decomposed into carbon monoxide and water.

Mercuric cyanide $Hg(CN)_2$ was first prepared by Scheele, in 1782, by boiling Prussian blue with mercuric oxide, and, in 1783, by dissolving mercuric oxide in hydrocyanic acid and evaporating to crystallisation. He also found that mercurous salts, when treated with soluble cyanides, yield mercuric cyanide and metallic mercury. The decomposition of the ferrocyanides, as already mentioned (p. 187), depends on the extremely small electrolytic dissociation of mercuric cyanide in aqueous solution. For the same reason, it is not decomposed by caustic alkalis, and hydrocyanic acid can only be expelled from it by boiling with a strong acid. The concentration of the mercury ions is, however, sufficient to permit of the precipitation of the extremely insoluble mercuric sulphide by sulphuretted hydrogen.

Mercuric cyanide crystallises in anhydrous, colourless crystals of sp.gr. 4·0. The saturated solution contains 93 grams per litre at 20°, 111 grams per litre at 25°; 100 grams of absolute alcohol dissolve 10·1 grams of it at 19·5°, and 100 grams of absolute methyl alcohol take up 44·2 grams at 19·5°.

Small quantities of mercuric cyanide are sometimes used in addition to alkali cyanide in the treatment of ores containing silver sulphide (Clennel, Cyanide Handbook, London, 1910, 297), the dissolution of which is accelerated, probably owing to the formation of mercuric sulphide

$$Hg(CN)_2+Ag_2S+2KCN=HgS+2KAg(CN)_2.$$

Calcium cyanide has never been prepared. An aqueous solution of lime in hydrocyanic acid decomposes completely into its constituents when boiled (Scheele). By evaporating such a solution *in vacuó*, Joannis obtained a crystalline compound, $3CaO·Ca(CN)_2,15H_2O$, which decomposed completely in a vacuum, leaving nothing but lime. Dry reactions, at high temperatures, yield calcium cyanamide, but no cyanide.

Barium cyanide $Ba(CN)_2$. When a concentrated solution, made by adding hydrocyanic acid to baryta in theoretical quantities, is evaporated *in vacuó*, crystals of the hydrate $Ba(CN)_2,2H_2O$ are deposited (A. Joannis, Ann. Chim. Phys. [5] 26, 484, 1882). This is a very deliquescent substance which, when dried *in vacuó* over sulphuric acid, yields an amorphous monohydrate which can be completely dehydrated by heating it very gradually to 100° in a good vacuum. The writer has failed to obtain a pure product in this way. Some 7 or 8 p.c. of the hydrocyanic acid escapes during evaporation, and the product contains a corresponding quantity of barium hydroxide. By drying pure $Ba(OH)_2,8H_2O$ in a good vacuum at 100°, a very finely divided powder of $Ba(OH)_2$ is obtained

which is suspended in dry light petroleum and treated with a small excess of dry hydrocyanic acid also mixed with light petroleum. In this way, the solid hydrated barium cyanide is obtained without evaporation:

$$Ba(OH)_2+2HCN=Ba(CN)_2,2H_2O.$$

When dehydrated *in vacuô*, it still contains a little hydroxide, but by shaking it with a little hydrocyanic acid and light petroleum and again drying, practically pure anhydrous barium cyanide is fairly easily obtained.

By saturating a solution of baryta in methyl alcohol with hydrocyanic acid, a compound $Ba(CN)(OCH_3)+CH_3OH$ is obtained, which, when heated, first loses methyl alcohol and then methyl ether, leaving $BaO+Ba(CN)_2$ (Drechsel, J. pr. Chem. [2] 21, 77, 1880).

Dry methods of preparation yield mixtures of cyanide and cyanamide. When barium ferrocyanide is heated it begins to decompose about 500°, yielding a mixture of barium cyanide and cyanamide (with carbon and iron) in which nearly 60 p.c. of the nitrogen is in the form of cyanamide, practically the same product as that obtained by the action of nitrogen on barium carbide. Even the action of cyanogen on barium amalgam yields a mixture (Drechsel), the reason being that barium cyanide decomposes into barium cyanamide and carbon, thus: $Ba(CN)_2=BaCN_2+C$. The change is very slow at 500° to 600°, but it is accelerated by iron (writer's unpublished experiments).

Barium cyanide is colourless; 100 grams of cold water dissolve about 80 grams of it (Joannis). It melts about 600°. It is distinctly volatile, even at its melting-point, but when mixed with barium oxide it is much less so.

Silver cyanide AgCN. The precipitate obtained by adding excess of silver nitrate to a solution of potassium cyanide is probably the silver salt of the complex acid $H[Ag(CN)_2]$. The solubility of silver cyanide in pure water lies between those of the chloride and sulphocyanide, as the following table shows:—

	Solubility at 25° in gram-mols. per litre
AgI	$0{\cdot}01\times10^{-6}$
AgBr	$0{\cdot}81\times10^{-6}$
AgSCN	$1{\cdot}08\times10^{-6}$
AgCN	$4{\cdot}40\times10^{-6}$
AgCl	$14{\cdot}10\times10^{-6}$

It is hardly attacked by cold dilute nitric acid, but is decomposed quantitatively on boiling (Plimmer, Chem. Soc. Proc. 1903, 285). It is slightly soluble in a solution of hydrocyanic acid, forming the unstable acid $HAg(CN)_2$. It dissolves very readily in alkali cyanides to salts such as $KAg(CN)_2$, in which the silver is contained in the complex anion $Ag(CN)'_2$. Owing to the excessively small dissociation of this anion, all silver salts except the sulphide are dissolved by cyanide solutions, and in presence of oxygen, metallic silver and the sulphide are also dissolved.

Gold cyanides. Aurous cyanide and the soluble aurocyanides are of technical importance. The former, AuCN, a yellow crystalline powder, insoluble in water and acids, is formed by the action of hydrocyanic acid on auric hydroxide. It is readily soluble in solutions of alkali or alkaline-earth cyanides, yielding aurocyanides such as $KAu(CN)_2$. A solution of the potassium salt, which is used for electroplating with gold, is readily obtained by precipitating a solution of gold chloride with ammonia and dissolving the fulminating gold in a solution of potassium cyanide, or by precipitating gold chloride with magnesia, dissolving out the excess of magnesia in the precipitate with nitric acid, and then dissolving the auric hydroxide in potassium cyanide as before.

Potassium aurocyanide is also formed when gold is dissolved in a solution of potassium cyanide in presence of oxygen or other oxidising agent:

$$4KCN+2Au+O+H_2O=2KAu(CN)_2+2KOH.$$

(Clennel, Cyanide Handbook, 1910, 10-32 gives a full account of the discovery of this reaction.)

The dissolution of metallic gold is primarily due to the great stability of the aurocyanogen ion $Au(CN)_2'$. Metals, like all other substances, have a tendency to dissolve in water. In contact with its aqueous solution, a salt will dissolve if the solution is unsaturated, or crystallise out if it is supersaturated. Metals behave similarly, with the important difference that they dissolve in the form of positively charged *ions*, so that when a metal is placed in contact with a solution containing fewer of its ions than correspond with equilibrium, it gives out positively charged atoms, becoming itself negatively charged, until the electrical attraction stops further change, and *vice versâ*. In this way, a definite potential difference always arises between a metal and a solution of it, the sign and magnitude of which depend on the nature of the metal and on the concentration of the positively charged ions of the metal in the solution.

In order for a metal to dissolve at all, therefore, it is necessary that the solution shall contain less than the saturation quantity of positive ions; and for the dissolution to continue, the positive charges of the ions and the negative charge of the metal must be got rid of in some way.

These conditions are fulfilled in the case of the dissolution of gold in a cyanide solution containing oxygen, because the dissociation of the complex ion, $Au(CN)_2' \rightleftarrows Au\cdot+2CN'$ is extremely small, and solutions of it therefore contain infinitesimal quantities of gold ion, and further the electrical charges produced by the dissolution of the gold are removed by the reactions:

$$Au\cdot+2(CN)'=Au(CN)'$$

and

$$O+H_2O+2(-)=2OH',$$

the result of which, written in the ionic form, is

$$4K\cdot+4(CN)'+2Au\cdot+O+H_2O+2(-) = 4K\cdot+2Au(CN)_2'+2OH'.$$

The potential difference between a metal like zinc (which has a greater tendency to dissolve than gold) and a cyanide solution is much greater than the natural potential difference between gold and the solution; hence gold ions are drawn out of the solutions to the zinc, where their positive charges are neutralised by the negative change of the zinc. This disturbs the equilibrium between zinc and the solution and also between aurocyanogen ions and gold ions, causing fresh quantities of zinc to dissolve and of aurocyanogen ions to dissociate, processes

which continue until the whole of the gold is precipitated.

As W. Skey (Trans. and Proc. New Zealand Inst. 8, 334, 1876) first showed, gold in cyanide solutions is electro-positive to silver and silver to mercury, so that gold will precipitate silver and mercury from their solutions in cyanides. This has been confirmed by Bodländer (Ber. 1903, 36, 3933). This reversal of the usual order is, as will be understood from the above explanation, due to the increasing stability of the mercury, silver, and gold complex cyanogen ions.

It is of interest to note that most of the minerals which accompany gold in its ores are electro-negative to gold in cyanide solutions, and therefore accelerate its dissolution in the way which is familiar in the solution of zinc in sulphuric acid in presence of copper or platinum.

Copper cyanides. When potassium cyanide is added to the solution of a cupric salt, a brownish precipitate of cupric cyanide $Cu(CN)_2$ is produced, which gradually evolves cyanogen, changing into green cupric cuprous cyanide. When heated, this loses a further quantity of cyanogen and yields white cuprous cyanide CuCN.

Cuprous cyanide is soluble in solutions of potassium cyanide, about 2½ molecules of KCN being required to dissolve 1 molecule of CuCN; the solutions contain the complex anions $Cu(CN)_3''$ and $Cu(CN)_4'''$ (Kunschert, Zeitsch. anorg. Chem. 41, 359, 1904). These anions are so little dissociated into copper ions that sulphuretted hydrogen will not produce a precipitate in the solutions, and therefore copper itself (in presence of oxygen) and all its compounds dissolve readily in cyanide solutions.

Zinc cyanide $Zn(CN)_2$ is a white substance, insoluble in water, but soluble in acids and in cyanide solutions. It is not easily prepared in a perfectly pure condition, because water decomposes it partially. When dry it is very stable, decomposing only at a bright-red heat.

The complex salt potassium zinc cyanide $K_2Zn(CN)_4$ crystallises in large well-formed octahedra from aqueous solutions; 100 grams of water at 20° dissolve 11 grams of it. It is anhydrous, and may be fused at a red heat without decomposition. The sodium salt $NaZn(CN)_3,2½H_2O$ is very readily soluble in water. The complex zinc cyanogen ions are much less stable than those containing copper, gold, silver, and mercury; a small excess of an alkali sulphide precipitates the zinc completely.

Cyanogen bromide CNBr. A solution containing cyanogen bromide in addition to a cyanide dissolves gold more rapidly than one containing cyanide alone (Sulman and Teed, Eng. Pat. 18592, of 1894; and J. Soc. Chem. Ind. 1897, 961). Cyanogen bromide is therefore used in the treatment of a few refractory ores, the West Australian tellurides especially. The final result of the reaction is expressed by the equation: $2Au+3KCN+BrCN=2KAu(CN)_2+KBr$.

Cyanogen bromide is formed by the action of bromine on a cyanide or on hydrocyanic acid. Owing to the difficulty of transporting either bromine or cyanogen bromide, it is always prepared at the place where it is to be used by liberating bromine from a mixture of a bromide and a suitable oxicising agent by the addition of sulphuric acid, and then adding a concentrated solution of an alkali cyanide. By the use of a suitable quantity of the oxidising agent, the whole of the bromine is utilised; with sodium bromate, for example, the reaction is (C. Göpner, Zeitsch. angew. Chem. 1901, 14, 355):

$$2NaBr+NaBrO_3+3NaCN+3H_2SO_4 = 3Na_2SO_4+3BrCN+3H_2O.$$

Cyanogen bromide is a colourless, crystalline substance which melts at 52° and boils at 61°; 100 grams of water dissolve from 5 to 6 grams of it at the ordinary temperature. It has an intensely irritating effect on the mucous membranes and eyes, and is said to be very poisonous. The perfectly pure substance can be kept without change, but traces of bromine (or hydrobromic acid) cause it to polymerise rapidly to cyanuric bromide, partial decomposition always occurring. It is very slowly decomposed by water: $CNBr+H_2O=HCNO+HBr$, the cyanic acid decomposing further to ammonia and carbon dioxide. Caustic alkalis bring about the same change instantaneously, alkali carbonates much more slowly, and bicarbonates have no action at all. Cyanogen bromide and potassium cyanide react in aqueous solution, yielding cyanogen; thus:

$$CNBr+KCN=KBr+C_2N_2$$

(private communication from Mr. C. J. Ellis). In solutions containing 0·2 to 0·8 p.c. of potassium cyanide and 0·1 to 0·2 p.c. of cyanogen bromide, the latter is completely decomposed in from 3 to 6 hours at the ordinary temperature.

Sulphocyanides or Thiocyanates. (Ger. *Rhodanide* or *Schwefelcyanide*.)

At the present time, sulphocyanides are obtained exclusively from the hydrocyanic acid of coal gas, but a modification of Gélis' synthetic process was working as recently as five years ago.

A. W. Hofmann (Reports by the Juries, Inter. Exhib. of 1862, 59-63), writing in 1862, said that ammonium sulphocyanide obtained by washing the spent oxide of gas works was only treated to recover its ammonia, the sulphocyanide being thrown away. In 1863 P. Spence (Eng. Pat. 2364, of 1863 (provisional only)) proposed to separate the sulphocyanides in gas liquor (after distilling off the ammonia) in the form of cuprous sulphocyanide by adding copper and ferrous sulphates, and the idea has been revived in various forms since that time, but it does not appear to have become of any importance. Gas liquor is really a very dilute solution of sulphocyanide, as the following figures, calculated from Linder's analyses of various English gas liquors (Chief Inspector of Alkali Works, 42nd Rep. 1905, 35), show:—

	Grams per litre				
	1	2	3	4	5
HCN as ferrocyanide	0·068	0	0·576	0·460	0
HCN as sulphocyanide	1·688	4·457	1·238	1·029	1·042
HCN as hydrocyanic acid	0·680	0	0·030	0·050	0·355

These liquors had all been stored for some time: perfectly fresh gas liquor contains ammonium sulphide and cyanide. By the action of the air, the former is oxidised to ammonium polysulphides, which convert the cyanide into sulphocyanide; thus:

$$(NH_4)_2S_2+NH_4CN=NH_4SCN+(NH_4)_2S.$$

The recovery of the whole of the hydrocyanic acid of coal gas in the form of a concentrated

solution of ammonium sulphocyanide is possible by applying this reaction in a suitable way. In 1877 W. Marriott (Eng. Pat. 3311, of 1877) proposed to scrub gas with a solution of sodium polysulphides, and in 1888 Campbell and Boyd (Eng. Pat. 10186, of 1888) proposed the use of manganese dioxide suspended in water. This liberates sulphur from a part of the sulphuretted hydrogen in the gas, and this free sulphur combines with ammonium sulphide to form polysulphide, which converts the cyanide into sulphocyanide. The final step, which led to a successful and economical process, was made by H. Wood Smith (H. Wood Smith, Gidden, Salamon, and Albright, Eng. Pat. 13658, of 1901) by simply scrubbing the gas through a suspension of sulphur, whereby the hydrocyanic acid is removed quantitatively, and a solution containing as much as 200 grams of ammonium sulphocyanide per litre may be obtained. This process is in use at several gas works, and yields practically the whole of the sulphocyanides made at present.

Synthesis of sulphocyanides from ammonia and carbon disulphide.—In Gélis' original process (A. W. Hofmann, Reports by the Juries, Inter. Exhib. of 1862, 59–63; A. Gélis, Eng. Pat. 1816, of 1860), a concentrated solution of ammonia and ammonium sulphide was agitated with carbon disulphide, yielding a solution of ammonium sulphocarbonate

$$(NH_4)_2S+CS_2=(NH_4)_2CS_3,$$

which was then heated to 90°–100° with potassium sulphide

$$2(NH_4)_2CS_3+K_2S=2KCNS+2NH_4HS+3H_2S.$$

A very large amount of sulphuretted hydrogen is produced in this way, the disposal of which would occasion much trouble and expense. Günzburg and Tcherniac (Eng. Pat. 1148, of 1878; 1359, of 1879; 1261, of 1881) heated a 20 p.c. solution of ammonia with carbon disulphide in autoclaves provided with stirrers at 100° until a pressure of 15 atmos. was reached, which indicated the end of the reaction. As Conroy (J. Soc. Chem. Ind. 1896, 15, 8) has shown, ammonium sulphocyanide is formed quantitatively under these conditions, the large pressure developed being due to the formation of the volatile ammonium sulphide $4NH_3+CS_2=NH_4SCN+(NH_4)_2S$.

Subsequent improvements were all in the direction of diminishing the quantity of ammonia required and reducing the pressure in the autoclaves. The simplest and most effective way of doing this is to add lime to the charge (Crowther and Rossiter, Eng. Pat. 17846, of 1893; Brock, Hetherington, Hurter, and Raschen, Eng. Pat. 21451, of 1893), the reaction then taking place in accordance with the equation:

$$2NH_3+2CS_2+2Ca(OH)_2 = Ca(SCN)_2+Ca(SH)_2+4H_2O.$$

A certain excess of ammonia over the quantity required by the equation must be used to prevent the formation of calcium sulphocarbonate. The excess of ammonia is distilled off, the residual mixture treated with carbon dioxide to remove sulphuretted hydrogen (in the way used in the treatment of Leblanc alkali waste), and the calcium carbonate filtered off. The clear solution of calcium sulphocyanide is easily converted into other salts.

The Principal Sulphocyanides.

Potassium sulphocyanide KSCN crystallises in anhydrous, striated prisms or needles of sp.gr. 1·9, which melt at 172·3°. It resembles saltpetre in appearance and taste. It is deliquescent and very soluble in water, 100 grams of which dissolve 177·2 grams at 0°, 217 grams at 20°, and 239 grams at 25°. It is also soluble in many organic liquids. The solubilities (in grams per 100 grams of solvent) are:

Acetone, 20·8 at 22°; 20·4 at 58°.
Ethyl acetate, 0·44 at 0°; 0·4 at 14°; 0·2 at 79°.
Amyl alcohol, 0·18 at 13°; 2·14 at 100°.
Pyridine, 6·75 at 0°; 4·97 at 58°, and 3·21 at 115°.

The fused salt becomes deep blue at 430°; the colour is said to be due to the liberation of sulphur. The sulphocyanides are plant poisons.

Ammonium sulphocyanide NH_4SCN crystallises in anhydrous, colourless leaflets of sp.gr. 1·3, which melt at 159°; 100 grams of water dissolve 122 grams at 0° and 162 grams at 20°; it is readily soluble in alcohol. When heated a little above its melting-point, it is partly converted into the isomeric thiourea. At 220° decomposition takes place, ammonia, sulphuretted hydrogen, and carbon disulphide being evolved, and guanidine sulphocyanide remaining behind.

Analysis of Cyanides.

The methods of analysis described here are those commonly employed in technical laboratories. It is believed that they will be found to be sufficient for most ordinary purposes.

Alkali cyanides. Owing to the hygroscopic nature of sodium and potassium cyanides when cold, samples, taken from different parts of a cake, should be transferred at once and without touching them with the hands to a hot iron mortar, broken up coarsely, and transferred to a hot perfectly dry bottle. If the sample has to be kept for any length of time before it is analysed, it is preferable to use glass-stoppered bottles and to grease the stopper with a little vaseline. Errors due to absorption of moisture in sampling are more common and more serious than those due to inaccuracies in testing.

Estimation of cyanogen.—5 grams of the sample are weighed out and made up to 500 c.c.; 25 c.c. of the solution are diluted to 200–300 c.c. and titrated with a solution of pure silver nitrate until the faintest visible turbidity results. The silver nitrate must be neutral and free from lead and zinc especially. A convenient strength of solution is obtained by dissolving 13·1 grams of silver nitrate in 1 litre of distilled water: 1 c.c. of this solution is equivalent to 0·01 gram of KCN. The solution is standardised by means of a solution of pure sodium chloride (dried by heating to redness before weighing) containing 4·487 grams per litre; 1 c.c. of the silver solution should exactly precipitate 1 c.c. of the sodium chloride solution using pure potassium chromate as indicator. In impure solutions of cyanides, the end point is often more easily observed if a little caustic soda (or a few drops of ammonia) and a crystal of potassium iodide are added before running in the silver nitrate solution. Sulphides interfere with the test, but they are easily removed by

shaking the solution with a little lead carbonate and filtering it.

Estimation of sulphide.—10 grams of the finely powdered sample are dissolved in 15 c.c. of ordinary water and a solution of lead nitrate (2·4 grams per litre) run in gradually. The mixture is stirred until the colloidal lead sulphide at first formed has coagulated into brown flocks; a drop of the solution is then placed on blotting paper beside a drop of the lead nitrate solution, and the two allowed to run together. When no difference can be detected between the colour of the paper where the drops have mixed and where they have not, the titration is considered to be at an end; 1 c.c. of the lead solution=0·001 gram of K_2S (T. Ewan, J. Soc. Chem. Ind. 28, 10, 1909; Rossiter, *ibid.* 30, 583, 1911).

Carbonate is conveniently estimated by precipitating a suitable portion of the solution with barium chloride in the cold (to avoid decomposition of cyanate). The precipitate is washed and titrated, together with the paper, with normal hydrochloric acid and methyl orange.

Chloride. The solution is neutralised with dilute nitric acid, and methyl orange, and boiled for about 1 hour (in a draught cupboard, of course) to drive off the hydrocyanic acid and decompose cyanate. The chloride remaining Richards and Singer, Amer. Chem. J. 27, 205, 1902) is then precipitated by a known excess of standard silver nitrate solution, the silver chloride filtered off and the excess of silver titrated with ammonium sulphocyanide and iron alum in the usual way.

If ferrocyanide is present, it may be precipitated with excess of silver nitrate in ammoniacal solution; by acidifying the filtrate with nitric acid, silver chloride is precipitated and may be weighed.

Cyanamide in presence of alkali cyanides is easily estimated by exactly neutralising the solution of 1 gram of the substance in 100 to 150 c.c. of water with *nitric acid*, and then boiling for 20 minutes to expel hydrocyanic acid. After cooling, 2 or 3 drops of ammonia are added, and then excess of silver nitrate. The canary-yellow precipitate of silver cyanamide Ag_2CN_2 is filtered off and dissolved in cold dilute nitric acid (which usually leaves a small residue of undissolved silver cyanide). The silver in the solution is then titrated by means of ammonium sulphocyanide, using ferric alum as indicator. The method is applicable to most substances containing cyanamide, the boiling with acid being, of course, omitted when little or no cyanide is present.

Cyanate. The solution is acidified with nitric acid and boiled for 20 minutes at least to expel hydrocyanic acid, and convert the cyanate into ammonium nitrate and carbon dioxide. The ammonia is then distilled off, after adding excess of caustic soda, and estimated by titration with *N*-hydrochloric acid as usual. In presence of cyanamide, the method is not available, because some ammonia is formed from the cyanamide when it is boiled with caustic soda. In this (rather uncommon) case, the cyanate must be estimated by collecting the carbon dioxide evolved when the sample is boiled with acid (Ewan, J. Soc. Chem. Ind. 1904, 23, 244).

Ferrocyanide is most conveniently estimated, either alone or in presence of cyanides, by titration with a standard solution of zinc sulphate until a drop of the solution no longer gives a blue colour when brought in contact with a drop of ferric solution on paper. A zinc alkali ferrocyanide of somewhat indefinite composition is precipitated, and H. G. Colman (Analyst, 33, 261, 1908; and J. Soc. Chem. Ind. 27, 806, 1908) has shown that the quantity of zinc solution required to precipitate a given quantity of ferrocyanide depends, to some extent, on the nature of the metal in the ferrocyanide used. This effect can be eliminated almost entirely by adding an excess of potassium sulphate. The method is carried out as follows: a solution containing 10·2 grams of $ZnSO_4,7H_2O$ and 10 c.c. of concentrated sulphuric acid per litre is standardised against pure potassium ferrocyanide; 25 c.c. of a solution of 10 grams of yellow prussiate per litre, mixed with 25 c.c. of a saturated solution of potassium sulphate, 25 c.c. of water, and 10 c.c. of 1:10 sulphuric acid, are convenient quantities. Subsequent titrations should be made as nearly as possible under the same conditions.

A more accurate method is that of W. Feld (Journ. für Gasbeleuchtung, 47, 565, 1903). Ferrocyanide, equivalent to 0·3 to 0·5 gram of yellow prussiate is boiled for 5 minutes with 10 c.c. of *N*-NaOH and 15 c.c. of 3 (molecular) *N*-$MgCl_2$. If cyanide is present, the boiling is continued for 10 minutes and the hydrocyanic acid may be distilled into caustic soda and titrated with silver nitrate with potassium iodide as indicator. 100 c.c. of boiling 0·1*N*-$HgCl_2$ are now run in, and the boiling continued for 10 minutes to convert ferrocyanide into mercuric cyanide. This is then distilled with 30 c.c. of 3*N*-sulphuric acid for 20–30 minutes, and the hydrocyanic acid collected in caustic soda and titrated as before.

The estimation of the valuable constituents of gasworks products (cyanide and ferrocyanide) is performed by triturating 30 to 40 grams of the material in a mortar with excess of a cold solution of caustic soda for several hours. A little ferrous sulphate may be added to convert cyanide into ferrocyanide. The filtrate is treated with 4 to 5 times its volume of methylated spirit. Carbonyl ferrocyanide (from 2 to 5 p.c. of the cyanogen is usually present in this form, but exceptionally as much as 20 p.c. may be present), sulphocyanide, sulphide, and excess of caustic soda remain in solution, whilst the whole of the sodium ferrocyanide is precipitated. The precipitate is then treated by one of the methods described above (H. G. Colman, Analyst, 33, 261, 1908; and J. Soc. Chem. Ind. 27, 806, 1908; F. W. Skirrow, *ibid.* 29, 319, 1910).

Sulphocyanide. Ferrocyanide, if present, is first removed from the solution by adding iron alum after acidifying slightly. The filtrate is treated with acid sodium sulphite in excess and then with copper sulphate and boiled for 1 or 2 minutes. The precipitate of cuprous sulphocyanide, which may be mixed with copper sulphide, is filtered off and washed with boiling water. It is then digested with excess of caustic soda which gives cuprous hydroxide and a solution of sodium sulphocyanide. This is separated by filtration, acidified with nitric acid,

and titrated with silver nitrate, using a ferric salt as indicator (Linder, 43rd Alkali Report, 1906, 39).

Alkali metals in commercial cyanides. 1 gram of the substance is evaporated to dryness with excess of hydrochloric acid. Traces of iron and calcium are removed by re-dissolving, adding a drop of ammonium carbonate, and filtering. The solution is again evaporated to dryness, and the residue is gently fused and weighed. The mixture of alkaline chlorides is dissolved in water and an aliquot portion titrated with silver nitrate, using chromate as indicator. If n gram of cyanide has yielded a gram of the pure mixed chlorides containing b gram of chlorine, the percentage of potassium in the cyanide is given by the formula

$$\left(\frac{2{\cdot}431a - 4{\cdot}012b}{n}\right)100.$$

This method is sufficiently accurate for most purposes, but the gravimetric estimation of the potassium as potassium platinichloride must be resorted to if a greater degree of accuracy is required. T. E.

CYANINE and **CYANINE DYESTUFFS** *v.* QUINOLINE COLOURING MATTERS.

CYANOMACLURIN *v.* JAKWOOD.

CYANOSINE *v.* TRIPHENYLMETHANE COLOURING MATTERS.

Iso-**CYANURIC ACID** *v.* FULMINURIC ACID.

CYCLOFORM. The trade name of *iso*butyl ester of *p*-amino benzoic acid used as a local anæsthetic. A white crystalline powder, m.p. 65°. Sparingly soluble in water (0·022 p.c.), readily soluble in alcohol and ether.

CYMENES. *Cymols.* The name *cymene* was first applied to the hydrocarbon isolated by Gerhardt and Cahours (Ann. Chim. Phys. [3] 1, 102 and 372) from Roman oil of cumin, which is the ethereal oil of *Cuminum cyminum*. Until 1891 this hydrocarbon was wrongly called *p*-methylpropylbenzene, but in that year Widman (Ber. 1891, 439, 970, 1362) proved it to be the *iso*propyl- compound (*see also* Fileti, J. pr. Chem. [2] 44, 150). Frequently, however, the various benzene hydrocarbons of the formula $C_{10}H_{14}$ are grouped together under the collective name of *cymenes*. No fewer than 22 of these are theoretically possible, of which 18 have been prepared; but only the most important, namely, cymene proper (*p*-methyl*iso*propylbenzene) and the tetramethylbenzenes are described here.

***p*-Methyl*iso*propylbenzene** (*Cymene*)

$(CH_3)_2CH{\cdot}C_6H_4{\cdot}CH_3$ (1, 4)

occurs in Roman oil of cumin (Gerhardt and Cahours, *l.c.*; Brühl, Ber. 1892, 149; Wolpian, Chem. Soc. Abstr. 1897, i. 357); in the volatile oil from the seeds of the water-hemlock (*Cicuta virosa*) (Trapp, Annalen, 108, 386); in the oil from *Ptycholis ajowan* (H. Müller, Ber. 2, 130); in oil of thyme (Lallemand, Annalen, 102, 119; Labbé, Bull. Soc. chim. 1898, [iii.] 1009) along with thymol $C_{10}H_{14}O$ and thymene $C_{10}H_{16}$; in eucalyptus oil (from *Eucalyptus Globulus*) (Faust and Homeyer, Ber. 7, 1429); in oil of caraway (Wolpian, Chem. Soc. Abstr. 1897, i. 17); in bitter fennel oil (Tardy, J. Pharm. Chim. 1897, 98); in oil of lemon grass (Barbier and Bouveault, Compt. rend. 121, 1159; Stiehl, J. pr. Chem. 1898, 51); in oil of origanum (Gildermeister, Arch. Pharm. 1895, 174); in geraniol (Semmler, Ber. 1891, 205); and in American petroleum (Mabery, Amer. Chem. J. 19, 419). May be obtained from camphor by abstracting from it the elements of water

$$C_{10}H_{16}O = C_{10}H_{14} + H_2O,$$

by heating it either with phosphorus pentoxide (Dumas, Ann. Chim. Phys. 50, 226; Delalande, *ibid.* [3] 1, 368) or with phosphorus pentasulphide (Pott, Ber. 2, 121), or with phosphorus pentachloride (Lippmann and Louguinine, Bull. Soc. chim. [2] 7, 374; *see also* Brühl, *l.c.*; Tiemann, Ber. 1895, 1089). Various isomerides of camphor yield cymene by the same treatment. The terpenes $C_{10}H_{16}$ may be converted into cymene by withdrawing two atoms of hydrogen: this may be effected in the case of oil of turpentine, for example, by distilling it with bromine (Oppenheim, Ber. 5, 94 and 628), or better, with iodine (Kekulé, *ibid.* 6, 437). Old turpentine generally contains cymene (Wallach, Chem. Zentr. 1898, i. 572; Kondakow and Schindelmeier, Chem. Zeit. 30, 722). It has been obtained synthetically from *p*-brom*iso*propylbenzene by means of methyl iodide and sodium (Widman, *l.c.*). To prepare cymene, camphor is warmed with an equal weight of phosphorus pentoxide, the cymene is poured off, treated again twice with a little phosphorus pentoxide, and finally rectified from sodium. The yield varies from 50 to 80 p.c. (Fittica, Annalen, 172, 307). It can also be prepared from *iso*propyliodide, and *p*-bromotoluene (Reuter, Chem. Zentr. 1892, i. 625; Brühl, *l.c.*) or from *iso*propylchloride, toluene and aluminium chloride (Silva, Bull. Soc. chim. [ii.] 43, 321).—Liquid boiling at 177°–177·5° (corr.); sp.gr. 0·8670 at 7·9°/4° (Perkin, Chem. Soc. Trans. 1896, 1125; 1900, 267). With chromic acid it yields paratoluic acid ($CH_3{\cdot}C_6H_4{\cdot}CO_2H$) and terephthalic acid

$C_6H_4(CO_2H)_2$ (1, 4);

with potassium permanganate, hydroxy*iso*propylbenzoic acid,

$(CH_3)_2C(OH)C_6H_4{\cdot}CO_2H$ (1, 4).

Taken internally, it appears in the urine as cumic (*p-iso*propylbenzoic) acid

$(CH_3)_2CH{\cdot}C_6H_4{\cdot}CO_2H$ (1, 4).

The preparation of cumene (*q.v.*) from propylbromide, benzene, and aluminium chloride, and that of cymene from *p*-bromotoluene, normal propylbromide, and sodium (Fittig, Schäffer, and König, Annalen, 149, 331) were for a long time the cause of great confusion in ascertaining the constitution of members of the cumene and cymene groups, as it was not realised that in each case the propyl- group changed into the *iso*propyl- group owing to the temperature of the reaction not being regulated.

Tetramethylbenzenes:

1. *Consecutive tetramethylbenzene* (*Prehnitene*) $C_6H_2(CH_3)_4$ (1, 2, 3, 4). When sodium durene-sulphonate

$C_6H(CH_3)_4SO_3Na$ (CH_3- groups 1, 2, 4, 5, *v. infra*)

is dissolved in concentrated sulphuric acid and allowed to stand for 12 hours, prehnitene-sulphonic acid is formed. The mixture is diluted with water, saturated with barium carbonate, the barium salts converted into sodium salts, and these, by treatment with phosphorus

pentachloride and ammonia, transformed first into sulphonic chlorides and then into sulphonamides. Prehnitenesulphonamide is separated by means of its sparing solubility in alcohol, and is then hydrolysed by heating with concentrated hydrochloric acid to 170°, when it yields prehnitene (Jacobsen, Ber. 19, 1213). Also obtained by heating bromocumene

$C_6H_3Br(CH_3)_3(CH_3,Br,CH_3,CH_3$: 1, 2, 3, 4)

with methyl iodide, benzene, and sodium, in a sealed tube at 150° for 12 hours.—Liquid boiling at 204° (corr.); solidifies in a freezing mixture, and melts at −4°. Dilute nitric acid oxidises it to prehnitylic acid $C_6H_2(CH_3)_3CO_2H$.

2. *Unsymmetrical tetramethylbenzene* (*Isodurene*) $C_6H_2(CH_3)_4$ (1, 2, 3, 5). From bromomesitylene (*v.* CUMENES), methyl iodide and sodium in presence of benzene (Jannasch, Ber. 8, 356). Best by passing methyl chloride into a mixture of mesitylene and aluminium chloride:

$$\underset{(1,3,5)}{C_6H_3(CH_3)_3}+CH_3Cl = \underset{(1,2,3,5)}{C_6H_2(CH_3)_4}+HCl$$

(Jacobsen, Ber. 14, 2629).—Liquid boiling at 195°–197°; solidifies in a freezing mixture. With dilute nitric acid it yields *α-iso*durylic acid, *β-iso*durylic acid, and mesitylenecarboxylic acid, isomeric acids of the formula

$$C_6H_2(CH_3)_3CO_2H,$$

and dimethyl*iso*phthalic and dimethylterephthalic acids, isomeric acids of the formula $C_6H_2(CH_3)_2(CO_2H)_2$ (Jannasch and Weiler, Ber. 1894, 3441; 1895, 531); potassium permanganate ultimately converts it into mellophanic acid $C_6H_2(CO_2H)_4$ (1, 2, 3, 5).

Symmetrical tetramethylbenzene (*Durene*) $C_6H_2(CH_3)_4$ (1, 2, 4, 5). Occurs in coal tar (Schulze, Ber. 18, 3032). By the action of sodium on a mixture of bromopseudocumene ($C_6H_2(CH_3)_3Br$ (1, 2, 4, 5), methyl iodide and sodium (Jannasch and Fittig, Zeitsch. Chem. 1870, 161). From toluene and methyl chloride in presence of aluminium chloride (Friedel and Crafts, Ann. Chim. Phys. [6] I, 461). From *o-* or *p*-xylene, methyl chloride and aluminium chloride (Jacobsen, Ber. 14, 2629). From pseudocumene, methyl iodide, and aluminium chloride (Rügheimer and Hankel, *ibid.* 1896, 2173).—Crystalline mass, smelling like camphor; melts at 79°–80°, and boils at 189°–191° (Jacobsen). Yields by oxidation with potassium permanganate, finally pyromellitic acid

$$C_6H_2(CO_2H)_4 \text{ (1, 2, 4, 5).}$$

CYMOLS *v.* CYMENES.

CYMOPHENOL *v.* CAMPHORS.

CYPRIAN VITRIOL. *Copper sulphate* (*v.* COPPER).

CYSTINE, *β-disulphido-α-aminopropionic acid*

$HO_2C{\cdot}CH(NH_2){\cdot}CH_2{\cdot}S{\cdot}S{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CO_2H$,

first discovered by Wollaston in a urinary calculus (Phil. Trans. 1810, 223); is a product of proteid metabolism under certain pathological conditions (Blum, Beitr. chem. Physiol. Path. 1903, 5, 1; Wolf and Shäffer, Amer. J. Physiol. 19; Loebisch, Annalen, 182, 231; Niemann, *ibid.* 187, 101; Thiele, Trans. Path. Soc. 1907, 58, 255), which, according to Abderhalden (Zeitsch. physiol. Chem. 1903, 38, 557), are hereditary. Dreschel found cystine as a normal product of metabolism in the liver of horse (Arch. Anat. Physiol. 1891, 243) and porpoise (Zeit. Biol. 1896, 33, 85). It was found by Külz (*ibid.* 1890, 27, 415) among the soluble products of an artificial pancreatic digestion of fibrin; and is a constant product of hydrolysis of keratin (Mörner, Zeitsch. physiol. Chem. 1899, 28, 595); Buchtala (*ibid.* 1907, 52, 474) obtained the following percentages of cystine from the materials mentioned: human hair, 13–14·5; human nails, 5·15; horsehair, 7·98; horse's hoofs, 3·20; ox hair, 7·27; hoofs of oxen, 5·37; pigs' bristles, 7·22; pigs' hoofs, 2·17.

According to Folin (J. Biol. Chem. 1910, 8, 9), cystine is most readily prepared from wool by boiling it in a reflux apparatus for 5–6 hours with twice its weight of strong hydrochloric acid, or until it ceases to give the biuret reaction; on removing the free hydrochloric acid by the addition of solid sodium acetate, a dark heavy precipitate of cystine is obtained; this is purified by decolourising a solution in 3–5 p.c. hydrochloric acid with bone-black, and precipitating the cystine in the hot filtrate by hot concentrated sodium acetate solution.

The cystine of urinary calculus is identical with that obtained from protein hydrolysis (Rothera, J. Physiol. 1905, 32, 175; Alsberg and Folin, Amer. J. Physiol. 1905, 14, 54; Fischer and Suzuki, Zeitsch. physiol. Chem. 1905, 45, 405), and was proved to be *β-disulphido-α-aminopropionic acid*) by Friedmann (Beitr. Chem. Physiol. Path. 1902, 2, 433). This view of its constitution was confirmed by the synthesis of racemic cystine from ethyl monobenzoylserine, obtained by reducing ethyl formylhippurate, the product of the condensation of ethyl formate and ethyl hippurate. On heating ethyl monobenzoylserine with phosphorus pentasulphide, and hydrolysing the product, *cystein* is obtained, and this is readily converted into cystine by oxidation with air in an ammoniacal solution:

$H{\cdot}CO_2Et+NHBz{\cdot}CH_2{\cdot}CO_2Et$
$\rightarrow CHO{\cdot}CH(NHBz){\cdot}CO_2Et$
$\rightarrow OH{\cdot}CH_2{\cdot}CH(NHBz)CO_2Et$
$\rightarrow SH{\cdot}CH_2{\cdot}CH(NHBz){\cdot}CO_2Et$
$\rightarrow SH{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CO_2H$
$\rightarrow CO_2H{\cdot}CH(NH_2){\cdot}CH_2S{\cdot}S{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CO_2H$

(Erlenmeyer, Ber. 1903, 36, 2720). Fischer and Raske (*ibid.* 1908, 41, 893) also obtained *r*-cystine from *dl-α*-amino-*β*-chloropropionic acid hydrochloride by heating it with barium hydrosulphide at 100° in sealed tubes, and oxidising the product by atmospheric oxygen in the presence of ammonia. From the natural *l*-serine the authors obtained, by a similar process, an optically active cystine which is identical with the *l*-cystine obtained from natural sources.

Cystine crystallises in thin colourless hexagonal plates; it has no melting-point, but decomposes slowly at 258°–261° (Neuberg and Mayer, Zeitsch. physiol. Chem. 1905, 44, 472). It is sparingly soluble in water, insoluble in alcohol or acetic acid, soluble in acids or alkalis. The cystine molecule contains two asymmetric carbon atoms, and *lævo*-cystine, the naturally occurring variety, has $[\alpha]_D$ −97·5° in ammonia, or −223° in hydrochloric acid solution (Gaskell, J. Physiol. 1907, 36, 142). *l*-Cystine is converted to the extent of 50 p.c. into *r*-cystine by heating with excess of hydrochloric acid of sp.gr. 1·124, at 165° for 12–15 hours; this decomposes at the

same temperature as the active isomeride, is three times as soluble in water, and can be resolved into the active components by the action of *Aspergillus niger*, the *l*- compound being consumed.

Cystine is readily reduced to *cystein* (*α-amino-β-thiolpropionic acid*) $HS{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CO_2H$ (Baumann, Zeitsch. physiol. Chem. 1882, 8, 300; Mauthner, Zeit. Biol. 1901, 42, 176), which can be converted by the action of bromine water into *cysteic acid* (*α-amino-β-sulphopropionic acid*) $HO_3S{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CO_2H$, and from this, by loss of carbon dioxide, *taurine* $NH_2{\cdot}CH_2{\cdot}CH_2{\cdot}SO_3H$ is obtained (Friedmann, Beitr. Chem. Physiol. Path. 1902, 2, 433). According to Von Bergmann (*ibid.* 1903, 4, 92), the normal taurine in the bile originates from the cystin groups contained in the ingested protein. Cystein yields cystine on oxidation, the change occurring spontaneously in alkaline solution, although the rate is increased by the addition of a mixture of ferric chloride and potassium cyanide (Mathews and Walker, J. Biol. Chem. 1909, 6, 289).

When cystine is given with food, it is completely oxidised to sulphate and excreted as such (Rothera, J. Physiol. 1905, 32, 175). Baumann and Preusse (Zeitsch. physiol. Chem. 1881, 5, 309; Ber. 18, 258) found that when bromobenzene was administered to animals, it was excreted as *bromophenylcystein*

$$CO_2H{\cdot}CH(NH_2){\cdot}CH_2{\cdot}S{\cdot}C_6H_4Br,$$

a compound crystallising in glittering needles or plates; m.p. 180°–182°, and yielding a blue crystalline *copper salt* $(C_9H_9BrSNO_2)_2Cu$.

Derivatives.—Cystine forms sparingly soluble salts with *copper*, $C_6H_{10}O_4N_2S_2Cu$; or *mercury*,

$$C_6H_8O_4N_2S_2Hg_2{,}HgCl_2;$$
$$2C_6H_{10}O_4N_2S_2Hg{,}HgCl_2{,}7H_2O;$$
$$2C_6H_8O_4N_2S_2Hg_2{,}Hg(NO_3)_2.$$

Benzoylcystine $C_6H_{10}O_4N_2S_2Bz_2$, m.p. 156°–158°, crystallises in needles and forms a sparingly soluble sodium salt (Goldmann and Baumann, Zeitsch. physiol. Chem. 1888, 12, 254). *Cystine-phenylhydantoin* is a well-defined crystalline compound, and is used for identifying cystine. *Cystine ethyl ester hydrochloride*

$$S_2[CH_2{\cdot}CH(NH_2){\cdot}CO_2Et]_2{,}3HCl$$

forms colourless needles, m.p. 185°, with decomposition (Friedmann, Beitr. Chem. Physiol. Path. 1902, 3, 1). Numerous *acyl-* derivatives of cystine have been described by Fischer and Suzuki (Zeitsch. physiol. Chem. 1905, 45, 405; Fischer and Gerngross, Ber. 1909, 42, 1485). Of these *di-l-leucyl-l-cystine*

$$S_2[CH_2{\cdot}CH(CO_2H)NH{\cdot}CO{\cdot}CH(NH_2)C_4H_9]_2$$

is a granular powder, turns yellow at 200°, and decomposes at a higher temperature, has $[\alpha]_D^{20}$ −136·6°, or, when obtained in a crystalline form, has $[\alpha]_D^{20}$ −141·4°; it gives a reddish-violet colour with copper sulphate; is precipitated by ammonium sulphate, and may be termed an *albumose*. M. A. W.

CYTISINE *v.* VEGETO-ALKALOIDS.

D

DAGUERREOTYPE *v.* PHOTOGRAPHY.

DAHLIA. Syn. *Hofmann's violet*, *Primula* (*v.* TRIPHENYLMETHANE COLOURING MATTERS).

DAHMENITE *v.* EXPLOSIVES.

DAMASCENINE *v.* VEGETO-ALKALOIDS.

DAMMAR RESIN, DAMMARYL, DAMMARYLIC ACID *v.* RESINS.

DANDELION ROOT. *Taraxaci radix.* (*Pissenlit*, Fr.; *Löwenzahnwurzel*, Ger.) The root of the common dandelion, *Taraxacum officinale* (Weber) (Bentl. a. Trim. 159), is used in medicine for its mild laxative and tonic properties. It is administered either in the form of expressed juice or weak spirituous extract. The roots employed should be collected in the autumn. (For a summary of the earlier chemical examinations of the root, *see* Pereira, Mat. Med. 1853, [2] 1574.) According to Kromayer (Arch. Pharm. 105, 6), there separates from the milky juice on standing a coagulum, 'leontodonium,' from which hot water dissolves a bitter substance. The bitter compound is removed from the solution by animal charcoal, from which it is extracted by alcohol, and after further purification constitutes the *taraxacin* of Kromayer. A similar taraxacin in warty crystals had been previously described by Polex (Arch. Pharm. 19, 50). From that part of the coagulum left undissolved by the water, alcohol extracts crystalline *taraxacerin* $C_6H_{16}O$ (Kromayer).

Among the other constituents of the root are *inulin* (Frickinger, Rep. Pharm. 23, 45; Widemann, *ibid.* 43, 281; Overbeck, Arch. Pharm. 23, 240) and *levulin* (Dragendorff, Sachsse's Farbstoffe, 125). Mannite, which had been often found in the juice, was shown by T. and H. Smith not to pre-exist in the root, but to be a product of fermentation (Pharm. J. 8, 480). In the root collected in October Dragendorff found 24 p.c. of inulin, while that collected in March contained only 1·7 p.c. associated, however, with 17 p.c. of uncrystallisable sugar and 19 p.c. of levulin. The last-mentioned compound is an isomeride of inulin, being distinguished by its solubility in cold water, the sweetness of the solution, and by the absence of any action on polarised light.

The leaves and stalks, but not the root of the dandelion, contains *inosite* (Marmé, Annalen, 129, 222). A. S.

DAPHNETIN. Daphnetin is present in the form of its glucoside daphnin in the bark of the *Daphne alpina* (Linn.) and *D. Mezereum* (Linn.).

The alcoholic extract is digested with boiling water, filtered, and treated with lead acetate solution. The precipitate is removed, basic lead acetate added to the filtrate, the lead compound of the glucoside decomposed with sulphuretted hydrogen, and the solution evaporated (Zwenger, Annalen, 115, 8).

Daphnin $C_{15}H_{16}O_9,2H_2O$ crystallises in prisms, melting at 200°, and dissolves in alkaline solutions, with a yellow colour. It is hydrolysed by boiling dilute acids with formation of daphnetin and glucose:

$$C_{15}H_{16}O_9+H_2O = C_9H_6O_4+C_6H_{12}O_6.$$

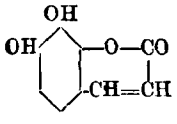
Daphnetin $C_9H_6O_4$ forms pale-yellow needles, is soluble in alkalis, with a yellow colour, and gives a yellow precipitate with lead acetate solution. On acetylation, a *diacetyl-* derivative $C_9H_4O_4(C_2H_3O)_2$ is obtained, and by means of ethyl iodide a *diethyl* ether $C_9H_4O_2(OEt)_2$ is produced. When daphnetin diethyl ether is boiled with caustic soda solution, the diethyl ether of daphnetinic acid

$$(OEt)_2C_6H_2\begin{cases}OH\\CH=CH\cdot COOH\end{cases}$$

is probably produced in the form of its sodium salt, which when ethylated gives the triethyl derivative:

$$(OEt)_2C_6H_2\begin{cases}OEt\\CH=CH\cdot CO_2H\end{cases}$$

By oxidising daphnetinic acid triethyl ether *triethoxybenzaldehyde*, is formed, which is readily converted into triethoxybenzoic acid. The silver salt of this acid, when destructively distilled, gives pyrogallol triethyl ether. Daphnetin is accordingly a dihydroxycoumarin, and has the following constitution:—



(Will and Yung, Ber. 1884, 17, 1081).

It has been synthetically prepared by heating pyrogallol with malic acid in the presence of sulphuric acid (Pechmann, Ber. 17, 933):

$C_4H_6O_5+C_6H_3(OH)_3=C_9H_6O_4+CO_2+2H_2O+H_2$

and by the condensation of pyrogallic aldehyde with sodium acetate (Gattermann and Koebner, Ber. 1899, 32, 287):

$C_6H_2(OH)_3\cdot CHO+CH_3\cdot COOH=C_9H_6O_4+2H_2O.$

Daphnetin is a yellow colouring matter, and gives with mordanted woollen cloth the following shades:—

Chromium	*Aluminium*	*Tin*	*Iron*
Olive yellow	Pale olive yellow	Very pale yellow	Olive black

(Perkin and Wilson, Chem. Soc. Trans. 1903, 83, 134) (*v.* LACTONES). A. G. P.

DAPICHO or ZASPIS. The South American name for the caoutchouc which exudes from the roots of *Hevea guianensis* (Aubl.).

DARWINITE *v.* DOMEYKITE.

DATE. The fruit of the date palm, *Phœnix dactylifera*. A palm of the tropics of Africa and the East Indies. It furnishes food to a large population in Egypt and Arabia.

The fruit grows in bunches of from 15 to 20 lbs. weight, and a tree usually produces about 20 bunches annually. The date palm also yields a sweet sap, which flows, when incisions are made in the trunk, almost continuously from November to March; the sap is clarified and boiled down, when a brown sugar, known as jaggery, is obtained (Bied. Zentr. 1884, 284).

Analyses of the flesh of dates give:

Water	Protein	Fat	Sol. carbohydrates	Fibre	Ash
28·8	1·9	trace	63·1	2·7	1·6

Dried dates, according to König, have the mean composition:

Water	Protein	Fat	Sugar	Free acid	Other carbohydrates	Fibre	Ash
18·5	1·9	0·6	67·2	1·3	4·3	3·8	1·8

Among the 'soluble carbohydrates' is included about 3 p.c. of pentosans, while the date stone contains about 2·7 p.c. of the same substances (Wittmann, Zeitsch. landw. Versuchs. Oesterreich. 1901, 4, 131).

König gives, as the composition of the date stone:

Water	Protein	Fat	Nitrogen free extract	Fibre	Ash
7·7	5·2	9·0	53·0	24·0	1·1

Dates are sometimes used as coffee substitutes, the whole fruit being occasionally employed, but more usually the stones only.

König gives as the composition of 'date-coffee':

Water	Protein	Fat	Sugar	Other carbohydrates	Fibre	Ash
6·6	5·5	7·9	2·2	48·7	27·8	1·3

yielding about 14 p.c. of its weight to water. H. I.

DATHOLITE *v.* DATOLITE.

DATISCA CANNABINA (Linn.). This is a tall, erect herb, resembling hemp, belonging to the *Datisceæ*, and met with in the temperate and sub-tropical Western Himalayas from Kashmir to Nepal. The root, known as *Akalbir*, is extensively used in Kashmir and throughout the Himalayas as a yellow dyestuff chiefly on alum-mordanted silk; but the colouring matter appears to be present in the whole plant, for the leaves and twigs can also be employed for the same purpose.

The leaves of the *Datisca cannabina* were first examined by Braconnot (Ann. Chim. Phys. [2] iii. 277), who isolated from them a crystalline substance which he named datiscin. Somewhat later it was shown by Stenhouse (Annalen, 1856, 98, 167) that this compound is a glucoside, and when hydrolysed is converted into a sugar, together with a yellow colouring matter, *datiscetin* $C_{15}H_{10}O_6$.

Schunck and Marchlewski (Annalen, 278, 261), however, considered that the formula $C_{15}H_{12}O_6$ was preferable, and showed that, on fusion with alkali, datiscetin gives *salicylic acid*. By the action of dilute nitric acid, a *nitrosalicylic acid* was produced, whereas with strong nitric acid, picric acid, as already indicated by Stenhouse, was formed. Datiscetin appeared to contain methoxyl groups, and was at that time considered by the authors to be most probably a xanthone derivative.

Korczynski and Marchlewski (Ann. d. Akad. Krakau, 1906, 95), have shown that pure datiscetin $C_{15}H_{10}O_6$ does not contain methoxy-groups. It consists of yellow needles, m.p. 268°–269°, soluble in alkaline solutions, with a yellow colour, and gives, with sulphuric acid, a yellow liquid possessing a green fluorescence. When boiled with strong alkaline solutions, phenol and salicylic acid are produced.

Tetraacetyldatiscetin $C_{15}H_6O_6(C_2H_3O)_4$ forms colourless needles, and melts at 138°; and *tetrabenzoyldatiscetin* $C_{15}H_6O_6(C_7H_5O)_4$ gives colourless needles, m.p. 190°–191°. Korczynski and Marchlewski consider that datiscetin is most probably a flavone derivative, isomeric with luteolin and fisetin.

Datiscin $C_{21}H_{24}O_{11}$ (S. and M.), the glucoside, crystallises in silky needles, which melt at about 190°, and dissolve in alkaline solutions with a yellow colour. Hydrolysis with dilute sulphuric acid yields datiscetin and *rhamnose*, not datiscetin and glucose, as stated by Stenhouse (*l.c.*).

The dyeing properties of datisca root on wool are very similar to those of old fustic. It is, however, slightly inferior in dyeing power. On cotton it dyes more like quercitron bark, in so far that the olives obtained on iron mordant are bluer in shade, as though some tannin matter were present. It appears to have about the same colouring power as quercitron bark, but gives a brighter yellow with aluminium mordant. Applied to wool, it differs from quercitron bark by giving with chromium mordant an olive-yellow, which is not of such a reddish tinge, and with tin mordant a bright yellow instead of an orange. It is an excellent dyestuff, and worthy to rank with the natural yellow mordant colouring matters at present in use (Hummel and Perkin, J. Soc. Chem. Ind. 1895, 14, 458).

A. G. P.

DATISCIN *v.* DATISCA CANNABINA.

DATISCETIN *v.* DATISCA CANNABINA.

DATOLITE. A native boro-silicate of calcium, discovered near Arendal, in Norway, by Esmark, in 1806. It derives its name from δατέομαι, 'to divide,' in allusion to its readily breaking with a granular fracture; Werner, however, incorrectly spelt it *Datholith*, whence it has been supposed that the name is connected with δάθος, 'turbid,' though the best-marked varieties are remarkable for their transparent vitreous character. The mineral crystallises in the monoclinic system, but occurs also massive, and a variety from Lake Superior, of opaque white colour, is so compact as to resemble unglazed porcelain. H. = 5 to 5·5; sp.gr. 2·8 to 3·4. Analyses agree closely with the formula $HCaBSiO_5$, corresponding with SiO_2, 37·6 p.c.; B_2O_3, 21·8 p.c.; CaO, 35·0 p.c.; H_2O, 5·6 p.c.

Datolite is occasionally found in the trap rocks of Scotland, especially in the Kilpatrick Hills. The finest crystals are found at Bergen Hill, New Jersey, and Westfield, Massachusetts. It occurs in veins of silver ore at Andreasberg in the Harz; in granite at Baveno, near Lago Maggiore; in serpentine at Monte Catini in Tuscany, and in the Lizard district in Cornwall; and in amygdaloidal melaphyre at Theiss in Tyrol, and many other localities. A botryoidal variety, from Arendal in Norway, containing as much as 8·6 p.c. of water, is distinguished as *Botryolite*. At Haytor in Devonshire, a rare pseudomorph was formerly found, consisting of large crystals of datolite completely replaced by quartz; this mineral is known as *Haytorite*. (For an exhaustive description of datolite, with bibliography, *v.* O. Lüdecke, Ueber Datolith: eine mineralogische Monograph, Zeitschr. f. Naturwiss. Halle, [4] 7, 1888, 235–403.)

F. W. R.

DATURA STRAMONIUM. *Thorn-apple.* (*Stramoine*, Fr.; *Stechapfel*, Ger.) The seeds and leaves of *Datura stramonium* (Linn.) are employed in medicine for their sedative and narcotic properties. The former are administered in the form of tincture or solid alcoholic extract, and the latter are smoked as a remedy for asthma. According to De Candolle, the plant is indigenous to the neighbourhood of the Caspian Sea, whence it has spread throughout the temperate and warmer parts of the world (Flück. a. Hanb. 2nd ed. 459; Bentl. a. Trim. 192).

Like other drugs derived from the *Solanaceæ*, the physiological action of datura depends upon the presence of poisonous alkaloidal constituents. What appeared to be a single alkaloid, 'daturine,' was isolated by Geyger (Annalen, 7, 272). Von Planta (*ibid.* 74, 246, and 252), and subsequently Ladenburg (*ibid.* 206, 279) and Schmidt (*ibid.* 208, 196; Arch. Pharm. [3] 22, 329), have, however, proved that 'daturine' is a mixture of *hyoscyamine*, the alkaloid of henbane, and its isomeride *atropine*, originally obtained from belladonna. In belladonna atropine was supposed to exist together with hyoscyamine, but it has been observed that in the extraction of the alkaloids, the relative proportion of the one to the other depends upon the mode of working. With greater care, the yield of hyoscyamine is increased, and that of atropine diminished, and it is possible to obtain the whole of the alkaloid as hyoscyamine. This fact has been investigated by W. Will (Ber. 21, 1719), who finds that hyoscyamine may be easily converted into atropine by the action of alcoholic solutions of alkalis or by heat alone. It is probable, therefore, that in belladonna, and possibly also in datura, hyoscyamine only is present in the plant, and that it is converted more or less into atropine during the process of extraction (*cf.* Schmidt, Ber. 21, 1829; Will and Bredig, *ibid.* 21, 2777). Ladenburg, however, questions this view (*ibid.* 21, 3065).

Scopolamine is also present in the leaves and stalks of *Datura stramonium* (Schutte, Arch. Pharm. 229, 492; Beckurts, Chem. Zentr. 1906, ii. 916).

The seeds yield about one-quarter of their weight of a bland fixed oil, from which Gérard (Compt. rend. 111, 305) has isolated *daturic acid* $C_{17}H_{34}O_2$. It consists of slender needles, which melt at 55°. Two other acids have also been isolated (Holde, Chem. Zentr. 1902, ii. 1417). (For a method of estimation of the alkaloids, *see* Schmidt, *ibid.* 1900, i. 376; Andrews, Chem. Soc. Trans. 1911, 99, 1871).

Other species of datura have been investigated by Van den Driessen Mareeuw (*ibid.* 1899, i. 539); Kucher, Arch. Pharm. 243, 309; Schmidt, *ibid.* 244, 66; Pyman and Reynolds, Chem. Soc. Trans. 93, 2077; Andrews, *l.c.*).

A. S.

DATURIC ACID $C_{16}H_{33}COOH$ occurs as a glyceride in the oil from the seeds of *Datura stramonium* (Gérard, Ann. Chim. Phys. [6] 27, 555); m.p. 55°.

DATURINE *v.* DATURA STRAMONIUM.

DAUCINE *v.* VEGETO-ALKALOIDS.

DEAD DIPPING. The process of producing a pale-yellow dead surface on ornamental brasswork. The brasswork, after the final stamping, with its adhering black scale from the annealing

oven, is placed in dilute nitric acid until the scale is detached, when it is removed and washed with water. It is next plunged into stronger nitric acid, and when its surface is covered with minute gas bubbles, it is washed in a solution of argol and dried in hot sawdust.

DEAD OIL. The higher boiling fractions of shale oil, from which the greater portion of the solid paraffin has been crystallised out.

***n*-DECAHEXANEDICARBOXYLIC ACID** $CO_2H[CH_2]_{16}CO_2H$. Prepared by the electrolysis of an aqueous solution of the potassium salt of the monoethyl ester of suberic acid, and hydrolysing the diethyl ester thus formed (Brown and Walker, Annalen, 261, 125); m.p. 118°.

DECAMETHYLENEDICARBOXYLIC ACID $CO_2H{\cdot}[CH_2]_{10}{\cdot}CO_2H$. Prepared by heating the methyl ester of bromundecylic acid with alcohol and potassium cyanide, and hydrolysing the product with alcoholic potassium hydroxide (Nördlinger, Ber. 1890, 2357); m.p. 124·5°–125·5°.

DECATOIC ACIDS $C_{10}H_{20}O_2$.

1. *Capric acid* $CH_3(CH_2)_8COOH$ is found as a glyceride in the butter of the cow and goat, and in cocoa-nut oil, in association with caproic and caprylic acids. Many fusel oils also contain it (Fischer, Annalen, 118, 307; Grimm, *ibid.* 157, 264; Rowney, *ibid.* 79, 236), and it is found as *iso*amyl caprate in certain Hungarian wines, and is formed by the oxidation or distillation of oleic acid (Redtenbacher, *ibid.* 59, 45), and by heating octylacetoacetic ester with alcoholic potash (Guthzeit, *ibid.* 264, 5). A white crystalline substance of m.p. 31·3°; b.p. 268·4° (corr.); sp.gr. 0·8858 at 40°/4°; possessing a goat-like smell; insoluble in cold water, but slightly soluble in boiling water.

2. *Diisobutylacetic acid,*

$$[CH(CH_3)_2CH_2]_2CH{\cdot}COOH$$

Obtained by heating di*iso*butylmalonic acid (Bentley and Perkin, Chem. Soc. Trans. 1898, 62); b.p. 225°–230° (730 mm.).

DECHENITE *v.* VANADIUM.

DECOIC ACID, CAPRIC ACID *v.* DECATOIC ACID.

DÉGRAS, or SOD OIL, is the waste fat obtained in the chamoising process, and is used for currying purposes, *i.e.* dressing bark-tanned or chrome-tanned leather. The skins which are to be converted into chamois leather, are first 'limed,' the hair is then removed and the unhaired hides are 'drenched,' *i.e.* placed in a 'sour bath,' in which the free lime is neutralised through an acid fermentation setting in, caused by *Bacillus furfuris*. The skins are then stretched and well rubbed with whale oil, or cod (liver) oil, in the United States with Menhaden oil, and worked in 'stocks,' so as to become thoroughly saturated with the oil. The skins are then exposed to the air, and the process of rubbing with oil and stamping in the stocks is repeated until enough oil has been absorbed. By exposure to the atmosphere, a portion of the oil becomes changed, and is most likely converted into the glycerides of 'oxidised' acids. In order to promote the oxidation of the oil, the skins are heaped together in a warm room, and covered carefully with canvas, so as to keep the generated heat in the heap whereby a large proportion of the oil is converted into 'oxidised' oil. The bulk of the oil is expressed from the skins by pressure, the remainder of the oil retained by the skins being removed by one of the two following methods, known respectively as the English and German method, or the French method. In the English and German method, the skins are washed with alkaline lyes; the emulsion thus obtained is acidified with sulphuric acid, when the fatty matter separates and is skimmed off. This fatty substance forms the 'sod oil' of commerce. In the French method, the skins are 'stocked,' aired, and 'fermented' for a shorter period than in the English or German method, so that a large proportion of the oil can be obtained from the skins by steeping them in warm water, and wringing or pressing in hydraulic presses. The oil thus obtained is termed 'première torse moëllon.' The oil still retained by the skins is recovered by washing with alkaline lyes, as is done in the English and German method, and the fatty matter so recovered is usually added to the moëllon.

The most characteristic constituents of dégras are the oxidised fatty acids contained in it.

Dégras is largely admixed with fish oils, blubber oils, tallow of low quality, &c. According to trade custom, such products are considered as a genuine product. On the other hand, the numerous substitutes of dégras, or *artificial dégras*, which occur in commerce, consist of highly adulterated dégras, the adulterants being mineral oils, wool fat, or blown blubber oil, and rosin. J. L.

DELPHINE BLUE *v.* OXAZINE COLOURING MATTERS.

DELPHININE *v.* VEGETO-ALKALOIDS.

DELPHLEGMATOR. An apparatus used in fractional distillation. The term is also employed in distilleries for an apparatus for freeing alcohol from water (*phlegma*).

DELTAPURPURIN *v.* AZO- COLOURING MATTERS.

DENATURANTS. This term is applied to substances which are added to articles usually subject to revenue imposts, and primarily intended for human consumption (as spirits, tobacco, &c.) in order to render such articles unfit for human consumption, but without impairing their efficacy as raw material for use in various arts and manufactures. Articles thus 'denatured' may safely (from a revenue point of view) be released from revenue control without payment of duty.

The principles underlying the choice of suitable denaturants are mainly as follows:—

(*a*) They should be inexpensive, so as not to add materially to the cost of the denatured article;

(*b*) Their use should cause the minimum amount of inconvenience to the manufacturer, both in regard to his processes and the necessary revenue supervision involved;

(*c*) The denaturant should not be incompatible with the process of manufacture or the subsequent use of the denatured article;

(*d*) It should be of such a nauseous and repugnant character as to remove any temptation to would-be consumers of the denatured article; and

(*e*) The denaturant should have such a relation to the original article both in quantity and character as to preclude its removal from the mixture by any process which could be profitably carried out on a commercial scale.

In the United Kindgom the dutiable articles allowed to be denatured are *tea*, *tobacco*, *wine*, and *spirit*, the last being by far the most important, both by reason of the large amount of revenue derived from it, and the great variety and extent of its applications in the arts and manufactures.

Tea, before being admitted for consumption in the United Kingdom, is examined by the Customs under sect. 30 of the Sale of Food and Drugs Act, 1875, and, if found satisfactory, is passed on payment of duty; but if otherwise, it is refused admission as 'tea.' Since, however, it still possesses a certain commercial value as a raw product for the extraction of theine or caffeine (*v.* ALKALOIDS), the Commissioners of Customs and Excise usually permit it to be admitted for this purpose duty free, after it has been effectively denatured in such a way as to make it unsuitable for use as a beverage, but without interfering with its efficacy as a source of caffeine. The same applies to those teas which have been accidentally damaged and are voluntarily withdrawn by the importers from sale as 'tea.'

In the case of tea, the denaturing process consists in grinding and mixing the tea with lime and asafœtida in the proportions of 1 part of asafœtida and 100 parts of lime to 1000 parts of tea.

Tobacco is dutied on the whole leaf, of which certain portions, as the midribs or so-called 'stalks,' are by manufacturers treated as waste or 'offal,' and the same applies to the unused portions of manufactured tobacco, known as 'shorts' or 'smalls.' On these the duty which has been paid is returned as 'drawback' to the manufacturer on condition, either that the tobacco offal is surrendered to the Government for destruction, or (if intended for such purposes as the manufacture of nicotine, insecticides, sheep dips, &c.), that it is denatured according to certain prescribed formulæ, and under the supervision of revenue officers. Denaturing is equally necessary in the case of offal from tobacco manufactured in bond (although no duty has been paid nor drawback given), in order to prevent its fraudulent use as a substitute for duty-paid tobacco.

The following formulæ have been officially approved in the United Kingdom for denaturing certain preparations having tobacco as a basis:—

(*a*) *Sheep wash.* To every 100 lbs. of tobacco are added 10 lbs. of blue vitriol, 15 lbs. of common salt, 2 lbs. of oil of turpentine.

(*b*) *Tobacco extract* manufactured in bond may be denatured by adding 30 parts of soft soap to 70 parts of extract.

(*c*) *Hop powder.* To every 75 lbs. of snuff or tobacco are added 28 lbs. of sulphur, 5 lbs. of asafœtida, and 3 lbs. of sago flour.

(*d*) *Fumigant* for horticultural purposes. To every 100 lbs. of tobacco or snuff are added 10 lbs. of ground hellebore, 18 lbs. of saltpetre, 6 lbs. of asafœtida, 4 lbs. of cayenne, 2 lbs. of lampblack, 10 lbs. of sago flour.

Wine which has become unsound and sour (owing to the formation of acetic acid) so as to be no longer suitable for use as a beverage, is released from revenue custody after being denatured with a view to its conversion into wine vinegar. The denaturant used in this case is 20 p.c. of commercial vinegar, or an equivalent quantity of acetic acid.

(For methods of denaturing alcohol, *v.* *Methylated spirits* and *Industrial alcohol*, art. ALCOHOL.) J. C.

DENITRIFICATION *v.* FERMENTATION AND SOILS.

DENSIMETER *v.* SPECIFIC GRAVITY.

DERMATOL. *Bismuth subgallate* (*v.* BISMUTH, ORGANIC COMPOUNDS OF; *also* SYNTHETIC DRUGS).

DERMOL. *Bismuth chrysophanate.* A yellowish-brown powder, said to have the composition $Bi(C_{15}H_9O_4)_3Bi_2O_3$. According to Merck, it is a mixture of impure chrysarobin and bismuth hydroxide (*v.* BISMUTH, ORGANIC COMPOUNDS OF; and SYNTHETIC DRUGS).

DERRIS ULIGINOSA (Benth.). The stem of this species of derris, used in the Far East as a fish poison, contains a poisonous resin (Proc. Amer. Pharm. Assoc. 1902, 50, 296).

DESCLOIZITE. A basic lead and zinc vanadate $(Pb,Zn)_2(OH)VO_4$, crystallising in the orthorhombic system, and isomorphous with olivenite (basic copper arsenate). A small amount of copper is sometimes present. The small crystals are deep reddish-brown in colour, and the streak is a paler yellowish-brown. It occurs in veins of lead ore in association with vanadinite, &c., and has been mined to a limited extent in New Mexico and Arizona, as a source of vanadium. Recently the mineral has been found in considerable quantities at Broken Hill in North-Western Rhodesia.

L. J. S.

DESICCATION AND DRYING. The removal of mechanically admixed water from substances. The removal of chemically combined water is usually termed *dehydration*, but it is not always possible to draw a sharp distinction between the two processes.

A substance may be termed 'dry,' even though it still contains mechanically admixed water, provided that this water is not apparent to the touch; the term 'desiccation' refers, strictly speaking, to the complete removal of admixed water.

The importance of drying and desiccating will be appreciated by a consideration of the numerous reasons for which these processes have to be employed, among which the following may be mentioned:—

1. To preserve material from undergoing physical and chemical alterations, *e.g.* leather, tobacco, fruit.

2. To remove water needed in preceding operations, *e.g.* drying coal after washing, woollen and cotton goods after dyeing, &c.

3. To facilitate accurate sampling, since substances are much more readily and uniformly mixed in the dry state than in the moist condition.

4. To diminish the weight of an unnecessary ingredient and thereby diminish cost of packing, carriage, and freight; *e.g.* timber, peat, &c.

5. To retain desirable moisture in a substance by drying its surface, thereby rendering the outer layer impervious to moisture, *e.g.* the drying of soaps and chocolates.

6. To prevent injury to health or goods, as in the case of the moisture-laden air of textile factories, evaporating rooms, &c.

7. To prevent waste of heat in vapourising water when combustibles are burnt.

A slight consideration of the various purposes served by drying processes is sufficient to bring out the wide range of degrees of dryness, and the various conditions to which the term 'dry' is applied. This vagueness arises partly from the difficulty of stating quantitatively the amount of water present in a given instance, and partly owing to the varying capacity that substances possess for absorbing moisture. Thus it is that in ordinary conversation substances are variously described as 'soaked,' 'wet,' 'moist,' 'damp,' 'dry,' 'dried,' 'desiccated' or 'dehydrated,' in order to indicate qualitatively their degrees of dryness.

The drying processes in use may be classified under the following headings, corresponding with the degrees of drying to which they lead :—

A. Gravitational drying, by draining, filtering, absorbing, and condensing.

B. Mechanical drying, by pressure and centrifugal force.

C. Drying by evaporation.

A. Gravitational drying. The processes included under this heading are usually only preliminary to the employment of method C above.

Drainage is a natural process occasionally used for the purpose of removing surface water, *e.g.* from washed coal. The procedure requires no special description.

Decantation is a process by which solid substances mixed with a large amount of water are separated from the greater portion of that liquid by allowing them to settle, and running off the liquid from above the sediment. In practice it is often the custom to arrange 'settling tanks' in series, stepwise, and gradually feed the mixture of liquid *plus* suspended solid into the upper vessel by means of a pipe leading to the bottom. The overflow runs into the second vessel, and so on throughout the series. Arrangements are provided for emptying each tank as required. China clay, chalk, and barytes are separated in this manner.

Filtration is a process of accelerated drainage. Thus wet pigments prepared by precipitation are drained on calico sheets stretched loosely over a skeleton framework. Filtration is greatly accelerated by partially exhausting the air from the chamber into which the liquid drains. A vacuum filter has been designed to work continuously, and consists of a hollow drum, mounted with its axis horizontal, and partly submerged in a tank containing the suspension to be filtered. The periphery is covered with filter cloth, and the water is drawn by suction, applied to the interior of the drum, through this cloth, leaving the solid matter as an outside coating. By slowly revolving the drum, a continuous coating of solid is thus formed, and, after it reaches a certain thickness, an adjustable skimmer removes the surplus. This arrangement can be adapted to many drying operations, and consumes very little power.

Absorption is a drying process in which the material is dried by causing it to yield its moisture to other substances which are capable of annexing it. This process is not often applied on a large scale, although it is commonly employed in the laboratory. Instances are furnished, however, in the preliminary drying of large clay ware in dried plaster of Paris moulds, and in the drying of the highly water-laden atmospheres of evaporating rooms, dye houses, &c., by pumping warm, fresh air into them. Warm air having a much higher capacity for holding water vapour than cold air, the result is naturally to effect a drying of the atmosphere, besides warming up the room and fittings.

In the laboratory, substances are frequently dried by placing them in a *desiccator*. This is simply a closed glass vessel containing in a suitable receptacle some chemical compound, such as anhydrous calcium chloride, concentrated sulphuric acid, or phosphoric anhydride, which has a remarkable affinity for water, so that it will, by absorption, remove water vapour from the interior even when the tension of the aqueous vapour therein is exceedingly small. The substance to be dried being placed in the desiccator, in the interior of which the tension of aqueous vapour is almost *nil*, it gives off its moisture, and this is continuously absorbed by the desiccating agent employed. The latter must expose a large surface for rapid absorption to occur. The velocity of drying in a desiccator may be greatly increased by exhausting the air from the interior (vacuum desiccator), since the rate at which moisture can diffuse from the material to the absorbing agent is thereby largely augmented. The degree of drying attained cannot, however, be increased, since that is limited merely by the pressure of the aqueous vapour when it has reached equilibrium with the absorbing agent. The rapidity of drying is also increased by placing the material to be dried at the bottom and suitably arranging the desiccating material above it. This arises from the fact that moist air has a smaller density than dry air at the same temperature and pressure; consequently, the natural process inside the desiccator is for the moist air to rise. The error in design exhibited in most laboratory desiccators, in which the above arrangement is reversed, was pointed out by Hempel (Ber. 1890, 23, 3566), to whom the desiccator shown in Fig. 1 is due. In this desiccator, the drying agent is placed in the trough of the lid.

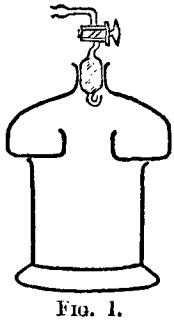


FIG. 1.

It is usual to evacuate laboratory desiccators by means of the water-pump, but it may be easily accomplished by simple chemical means (J. Amer. Chem. Soc. 1906, 28, 834; Amer. Chem. J. 1902, 27, 340).

Condensation.—This is employed as a means of drying materials which must be handled at low temperatures, and is a method adopted

in cold storages. The principle of the process is, briefly, that the moist air of the rooms is drawn out and passed into chambers maintained at a very low temperature, where it is made to deposit the greater part of its moisture as a liquid. The dry air is then returned to the drying rooms, either cold, when it warms itself at the expense of the materials drying, or after being previously heated. This circulation of air goes on continuously. The method adopted in order to maintain a low temperature in the cooling rooms is to allow liquid ammonia, carbon dioxide, or ether to evaporate at the requisite rate through long coils of metal pipes over the outer surfaces of which the moist air is drawn. The latent heat of the ammonia (or other) vapour is obtained at the expense of the heat of the moist air, which is thereby cooled; the vapour condenses on the pipes and the water trickles down into troughs and flows away. The ammonia (or other) gas is repeatedly used in a cycle of operations, being successively liquefied and evaporated. This process is highly efficient, but requires careful handling for economical working.

B. **Mechanical drying.** These methods are efficient when water forms a large proportion of the total weight, and when the solid material to be separated is porous in texture. They leave the solid damp or moist.

Drying by pressure.—There are very few cases in which direct mechanical pressure is used for removing water from substances, the most important of which is the direct squeezing of peat in specially designed machines, in order partly to remove the surplus water.

Filter presses are used for partly drying semi-solids, and leave them still containing about 20 p.c. of moisture. They are efficient in removing the large bulk of the water from granular substances in a state of thick mud. Essentially a filter press consists of a number of flat sections or chambers formed of iron plates covered with filtering cloths, and supported in a strong horizontal frame, in which they can be squeezed up tightly together. The chambers are made either round or square, and usually each has its own outlet cock, while the washing arrangement can be made reversible. The sludge to be filtered is fed in under moderate pressure, and all the outlet cocks opened. After water has ceased to flow out, the solid in the press is washed, if desirable, and the press then taken to pieces to remove the moist solid cakes from its interior. This process is used for filtering, among other things, sewage sludge, gold slimes, and precipitated pigments.

Drying by centrifugal force.—This method is largely employed for drying clothes in laundries, when the centrifugal machines are termed hydro-extractors. It is also used for drying wool, cotton yarns, piece goods, &c., after they have left the dye houses, and for separating and drying sugar, gun-cotton, and starch.

The process consists in placing the material to be dried in a basket containing numerous holes, and rotating it in a horizontal plane at a considerable speed. The water is thrown off from the material very effectually, much more effectually than when simple filtration or filtration under moderate pressure is adopted.

A centrifugal machine consists essentially of a circular basket, rotated on a vertical central shaft and enclosed in an outer stationary casing. The circular basket is drum shaped, having an open top to introduce the material and sometimes a valve at the bottom to form an outlet for dried crystals. The periphery is perforated with holes of a suitable size. These baskets are made of steel, bronze, copper, aluminium, silver, or china, as may be suitable, and are lined with rubber, enamel, or lead when dealing with acid liquids. The outer stationary casing serves as a guard in case of accident and as a collector for the water. The successful working of a centrifugal machine depends upon the skill with which the vertical shaft is mounted and driven, since the apparatus must have sufficient freedom when running for the axis to take up the position it requires; otherwise vibrations will rapidly wreck the machine.

C. **Drying by evaporation.** This is by far the most efficient method of drying; indeed, several of the preceding processes are only employed as preliminary steps to the application of this more powerful method.

Drying by evaporation is a process in which the water is removed by first converting it into vapour and then conveying the vapour away. Water always has a tendency to pass into the gaseous state, and is constantly giving off vapour from its free surface. If this process occurs in a closed space, some of the vapour finds its way back into the liquid, and a state of equilibrium is set up when the rate at which vapour is leaving the surface has become equal to the rate at which it is passing back into the liquid. To the state of equilibrium at any particular temperature there corresponds a definite vapour pressure, which is a measure of the tendency of water at that temperature to pass into the gaseous state, and this vapour pressure rapidly increases with rise of temperature. When evaporation takes place in free space, no condition of equilibrium is reached, since, owing to diffusion of the vapour, the rate at which it passes back into the liquid can never equal that at which vapour leaves it. Evaporation therefore goes on until no more liquid remains. From these considerations, it follows that the two main practical principles in drying by evaporation are: (i.) to warm the material and thereby increase the tendency of its contained water to vapourise; and (ii.) to remove the vapour as it is produced from the neighbourhood of the substance, in order that the evaporation shall proceed continuously.

In applying these principles it is necessary to bear in mind that the rate of drying permissible in any given instance is restricted by (*a*) the physical and chemical nature of the material, which put a limit to the rate at which heat may be safely applied; and (*b*) by the cost of drying, since the plant mechanically most sound may not be most economical in practice. It must always be remembered that the nature of the material governs the method of drying to be employed, and must be considered before the question of mechanical efficiency.

The various methods for applying heat and for removing vapour are indicated below, and in order to explain more definitely how these methods are employed in practice, brief

descriptions follow of various types of drying installations in actual use, and of the purposes for which they are used.

Application of heat. In the majority of cases hot air is employed for conveying heat to the material, and its use is attended with many advantages. Air, although an extremely poor conductor, is an excellent absorber of heat; the increase in volume resulting from this process naturally tends to disperse this heat and to warm surrounding materials by convection. The mobility of the air enables it to come into intimate contact with the surfaces of materials, thereby supplying the heat necessary to vapourise the moisture. Most important of all, the heated air can be thus supplied in large or small amounts, at any desired rate and at uniform pressure, while any of these factors may be rapidly and easily altered at will.

Of the various *sources of heat*, the cheapest is, of course, solar heat. Owing to its unreliability so far as quantity and continuity are concerned, its direct use is attended by considerable risks. Indirectly, however, it is of great value, in being the primary cause of natural air currents. Drying directly by furnace heat obtained by fuel combustion is economical, but the method is restricted in use to drying those substances which are not sensibly affected by high temperatures. For the commonest method of drying, by means of a warm blast of air, heat is usually supplied by passing the air over the surfaces of radiators. These are simply iron vessels, built to expose as much surface as possible, and through the insides of which steam, hot water, or hot gases are passed. Heat is conducted through the iron to the outer surface, and warms the surrounding air mainly by radiation.

The *dangers* encountered in the application of heat result from the nature of the material, and the factors involved, which are briefly discussed below, naturally affect various materials to very different degrees.

(*a*) Rate of application of heat. Although the amount of heat required to vapourise a definite quantity of water is fixed, yet if this heat be applied at a rate faster than that to which the material can accommodate itself, injury will result, *e.g.* wet bricks will crack unless the greater part of their water is first driven off at a slow and uniform rate.

(*b*) Change in power of absorbing heat with loss of water. As a material dries, its heat capacity usually diminishes, and hence the risk of overheating increases as drying progresses.

(*c*) Uncertainty as to degree of dryness, which is often unavoidable.

(*d*) Local application of heat. This is the usual cause of distortion and cracking, since most materials shrink as they dry, and local shrinking sets up strain. This makes it advisable to keep wet material from actual contact with the source of heat, and to agitate the material to continually expose fresh surfaces, since evaporation is a purely surface phenomenon.

Methods for removal of vapour. The natural method by which vapour is removed is by means of *air currents*, and, excepting in the case of the vacuum process, this is the method upon which all artificial processes for vapour removal are based.

The ordinary *atmospheric* process for drying utilises the natural movements of the air, *e.g.* by utilising the action of the wind on floors, pans, gantries, sheds, &c. It requires no motive power, but, being dependent upon varying atmospheric conditions, it is not reliable.

In the *exhaust* process the moisture-laden air is drawn away from the wet material quicker than gravity would perform the removal. For this purpose a propellor or fan is usually employed. Since the operation is carried out under slightly reduced pressure, vapourisation proceeds quicker than it otherwise would; on the other hand, the exhaust carries away the heat-bearing medium from the material to be heated, and unless proper control is exercised, this defect may more than counterbalance the increased rate of removal of vapour.

In the *vacuum* process the material is enclosed in an air-tight receptacle, from which the air may be exhausted to any desired extent. Heat is then applied, and the vapour pumped off as fast as it is produced. Considerable experience is necessary in the application of this process, which, properly applied, is highly efficient and rapid.

In the *plenum* process the vapour is removed by supplying sufficient warm air to create an augmentation in air pressure. A fan is usually employed for this purpose, and drying must, of course, take place in an enclosed room with regulated egress for the air. This process is usually the best to employ, since it can be maintained strictly under control.

Drying installations. Drying floors. *Natural floors* are not often used, since serious difficulties arise as to heating, handling the material, and removing the vapour. Haymaking affords a good instance of its employment.

Artificial floors warmed by the products of combustion from a furnace, by hot gases, or by steam passing in flues or pipes beneath, are a considerable improvement on natural floors. Advantage is taken in constructing them of any convenient sandy or porous ground floor; sand is put down if the natural ground is clayey.

These floors are used for drying china clay, calcium phosphate, barytes, chalk, cement, and calcined quartz, materials which are not readily injured by excessive or irregular heating.

Drying gantries or racks. These are employed in order that as much surface as possible may be exposed to air currents. Their construction assumes various forms. According to circumstances, they may be either skeleton shelves, or racks, or props, &c. Occasionally hot water or steam pipes are used as supporting racks, but their use is to be avoided as uneconomical, and tending to produce uneven drying and distortion.

Such substances as damp corn, peat, raw rubber, chalk, bricks, and clayware are frequently dried on open racks, while pigments in colour works are often dried in open gantries of skeleton shelves.

Drying sheds. These are merely drying floors or gantries provided with roofs to keep off rain and snow. These sheds are best constructed of light open framing in order to facilitate the removal of vapour, and the more open

it is on all sides the better, provided that the substance is not such that direct sunlight must be excluded from it, *e.g.* rubber. Such sheds are highly efficient in producing 'air-dried' materials. Bricks are often dried in sheds erected on drying floors, while Chile saltpetre is dried in sheds without the application of artificial heat, as also are china clay and ochre in the quarry state.

Drying pans and troughs. Drying pans, correctly designed and handled, are very useful appliances. The oldest commercial use of such pans is in the evaporation of salt brine, which, as usually carried out, is not at all an economical process. The pans are usually rectangular, and each stands in its own shed. They are directly heated, three or four fires being beneath each pan.

Shallow earthenware pans are of great use in the colour trade, the pigments being readily dried if the pans are carefully arranged on gantries in well-heated and ventilated chambers.

Semi-cylindrical iron pans heated from below by gas or steam give good results in drying soft materials, especially powders. They are most efficient when provided with revolving grids for mechanically stirring the wet material and with valve outlets at the bottom for automatically discharging their dried contents.

Granulated sugar is dried in a type of troughed pan, through which passes a hollow 'conveyer' carrying hollow paddles. Steam is blown through the conveyer and paddles. The trough is jacketed on one side, and through this jacket air is blown into the bottom of the trough. The sugar is fed into the hot end, and automatically carried by the heated paddles to the outlet at the cool end of the trough.

Kilns. These are buildings containing a furnace, the direct heat of which is used for drying materials by allowing the products of combustion to pass through them. For substances which may be strongly heated without damage, kiln-drying is an economical method of procedure, since the walls of the kiln are very effective in saving heat that would otherwise be lost; but care must be taken to provide proper exits for the vapour.

A primitive type of kiln is one in which calcium phosphate is dried. It consists of a plain rectangular brick building with a wooden roof. The floor is piled with wood, and the phosphate placed upon it. Flues admit air for combustion and circulation. Such a kiln will burn for from 2 to 5 days and dry from 1000 to 1200 tons of phosphate.

Kilns for drying clays, fuller's earth, barytes, and chalk are constructed upon the same principle, the fire being placed so as to prevent the ashes mixing with the material; the latter is sometimes supported within the kiln on iron racks.

A rotating bed dryer is in extensive use for drying materials which allow of direct firing. The material is placed on a circular cast-iron bed, which slowly rotates on a vertical shaft. The bed is covered by a firebrick arch, into which the exit flue leads. Heating is done directly by fires, and stationary blades fixed in the arch stir the material as it is drying. The blades are fixed at such an angle that the material is slowly moved from the centre, above which the feed is situated, to the edge, where it is automatically discharged. This is a common type of drying kiln for ores.

Drying cylinders. This term includes those dryers in which the material to be dried is contained in a cylindrical tube, which is slowly rotated. The essential feature of their construction is that the rotation of the cylinder affords the means of moving the material along. With suitable materials and the necessary power, cylinders will automatically deliver large quantities of uniformly dried product, with the minimum of labour and fuel consumption. They are consequently extensively used, and many types of drying cylinders have been devised.

For materials that withstand high temperatures, the heating may be carried out by passing the hot gases from a furnace through the tube. The latter is constructed of steel, and is mounted nearly horizontally (slope of 1 in 12), with the furnace at the lower end. The feed is situated at the higher cold end, and the gases pass out through a flue at this end, connected with a fan or chimney. As the material gravitates down the tube it is dried, and on reaching the lower end, it drops out, quite dry, into trucks. A modification of this construction consists in enclosing the steel tube in a horizontal brickwork chamber, and heating it externally by passing the furnace gases into this brickwork chamber, whence they pass through a series of external hooded openings into the steel cylinder itself. This arrangement allows of a more gradual and systematic heating, while dust and other objectionable parts of the products of combustion may be arrested prior to the gases entering the cylinders. Besides these two arrangements, many others have been devised, each having its particular advantages.

Cylinder dryers are very suitable for heating by steam, thus meeting the requirements of such substances as sugar, salt, soda, cocoa, coffee, &c., provided they contain not more than 25–30 p.c. of moisture. The drying cylinder may be either steam-jacketed externally, or internally, or by both methods united. The exhaust is best taken by means of a fan at the feed end of the cylinder. In using such dryers for sugar, they are employed in conjunction with a conveyer trough dryer (*v. supra*), into which the sugar falls after passing through the steam-heated cylinder.

Drying rollers. These are heated rotating cylinders, with the outside periphery of which the material to be dried is brought into contact. They are made of steel, cast iron, copper, or tinned iron, and are usually heated by passing steam or hot air through their interior. Another method of heating consists in coating the cylinder externally with felt and rotating it in a polished iron bed, against the under surface of which steam is blown. The material to be dried is automatically passed between the roller and its bed, and the rollers are usually arranged in series of two to eight.

The latter method is largely employed in laundry work, and the use of drying rollers is extensive in the paper and textile trades.

Drying tunnels. These consist essentially of a stationary passage through which the material passes either continuously or intermittently as the drying proceeds. Drying in a

tunnel is progressive from one end to the other. Heat may be applied either by direct firing or by heated air, which passes into the tunnel from beneath one end and travels along to the other. The warm air current usually travels in the opposite direction to that in which the material moves, but not always, as, for instance, in the drying of wool, where the pressure of the warm blast is utilised in blowing the material forward. The vapour-laden air may be removed either by chimney, exhaust, or by pressure fan, while the material may be handled in a very large number of ways, according to circumstances. This method of drying is economical, but the initial cost of plant is often considerable.

In drying timber, the material is carried on special trucks running on a tram track. The air is heated by means of a heater coil fed with steam and situated under the track at the discharging end. The air ascends, dries the timber, thereby becoming cooler and denser, and then, pressed forward by the incoming air, it gravitates into a large space beneath the feeding end of the tunnel and passes up the flue. Wool is dried in a tubular tunnel, being blown along by the warm air. Soap is dried by passing it on trolleys through narrow tunnels, usually arranged in fours, through which warm air is driven by means of a propeller. In particular, bricks and clayware are dried by passing them through drying tunnels, for which purpose a very large number of types of plant have been devised.

Drying rooms. These are enclosed spaces, which are warmed by means of hot air, and into which the loader or discharger has to enter. When not constructed of brick or stone, the material of the walls should be chosen for its insulating qualities.

The expense attached to drying by this method is due largely to the manual labour required in handling the material, which arises, in most cases, from the fact that the peculiar properties of the material render it impossible to utilise mechanical methods. Since manual labour in a heavily moisture-laden atmosphere is unhealthy, desiccation in drying rooms is restricted in practice to those materials for which the process is unavoidable. Such products as hops, confectionery, leather, paper, textile fabrics, pottery, and rubber are dealt with by this method.

The materials are supported in the most convenient manner within the chambers, and warm air circulated either through or over them. The warming of the air may be accomplished either within or without the compartment, by means of radiators, and, if desired, the same air can be used continuously in a circuit (compare the condensation process, p. 210).

Drying ovens. These are entirely enclosed drying chambers; the necessary heat for the purpose is not generated within them, neither is it necessary to enter them in order to charge or remove the material to be dried. Ovens can be adapted to suit a wide range of conditions, and some of the most scientific and economical dryers are of this type.

A great variety of methods are available for the purpose of heating, since the heat is generated outside the oven. Products of combustion are readily excluded from the material. There is no necessity for the plant to cool down before the dried product is removed, and hence heat losses are greatly minimised. Heat is applied to the material either by means of hot gases, usually hot air, or by direct conduction through metallic plates, as, for instance, in steam ovens. Vapour is usually removed mechanically, either by pressure or exhaust, but it may be pumped off, as, for instance, in all vacuum machines. Ovens are more efficient than drying rooms, since the latter are frequently used for other purposes than drying, whereas the former are designed exclusively for drying. Only a few types of drying ovens can be here described.

Laboratory ovens are rectangular boxes, constructed of copper, iron, or aluminium, which may be either steam- or air-jacketed, or in simple ovens not jacketed at all. The substances to be dried are supported on shelves inside. With air ovens heat is applied directly at the bottom of the oven or of the outer jacket. A ventilator situated at the bottom of the oven door allows air to enter, and one or more chimneys in the lid allow the warm vapour-laden air to escape. A convenient method of heating, which can be readily controlled, consists in heating electrically, by passing a current through a number of resistance coils embedded in the jacket surrounding the oven. (*See* also ANALYSIS, Vol. I.) Removable tray dryers are largely used for drying tea, coffee, cocoa, cinchona bark, &c. The trays are arranged in the oven in a series of rows. Each tray has a separate slide, and is independent of the others, and each column of trays has its own regulating damper for the hot air. The method of working is progressive, the wet material being first placed in the top tray of the column and passed downwards stepwise to the bottom. The heat required is supplied from a multitubular furnace, which also produces the air current which aërates the material. The hot air may be allowed to rise through the material, or be drawn down by two centrifugal fans on either side of the centre through the substance. The latter arrangement is more readily controlled, gives a larger output, and affects a considerable saving in height. A modification that gives an even larger output is that which consists in causing each horizontal line of trays, commencing with the lowest, to automatically tilt and discharge its contents into the base of the dryer. For drying other substances than those mentioned above, many other types of tray ovens have been devised.

Sliding-panel dryers are used in laundries, and can also be adapted for drying yarns, piece goods, &c. They consist of a row of vertical sliding panels, built up with hanging rods to form rigid horses for the goods. They are readily movable on runner wheels, and each panel may be withdrawn independently of the others, with the minimum loss of heat, as the back of the panel closes the outlet and thus reshuts the oven. A hot-air blast is supplied from above, and after passing through the oven it discharges into the open.

The Lennox plate-oven dryer is a type which has many advantages, is compact, and occupies a small floor space. The outer vertical cylindrical casing is built up in sections to allow for extension and renewal. A concentric cylindrical

drum slowly rotates inside. At each external section there is a horizontal metal plate within the apparatus, and each section plate contains a hole; these holes are not vertically above one another. The material to be dried is fed in at the top, falls on the first section plate, and is slowly stirred round by horizontal arms on the rotating centre drum till it reaches the hole in the plate, It then falls through on to the next plate, is slowly stirred round till it falls on to the third plate, and so on, till it is discharged at the base. Hot air is blown in at the base, and passes upwards into the central drum, from which it issues, through numerous holes in its sides, passes through the material, and thence upwards and outwards.

A horizontal steam-jacketed cylindrical oven, containing a very powerful and thorough agitating gear inside, is used for drying wet pasty materials like meat, fish, &c. The material is fed in at the top, and discharged as a dry, mealy powder through a manhole in the bottom. The vapour is removed from the interior through a large outlet duct operated either by a fan or pump according to circumstances. In vacuum ovens the removal of vapour by means of air or other gases in motion is discarded in favour of pumping away the vapour from the warmed-up material, operating in a closed space and diminishing the pressure within it to any desired extent. The oven must be strongly built, and all joints must fit tightly to maintain the diminished pressure. The material may be supported inside in any suitable manner, for instance, on steam-heated grids. The necessary accessories are a vacuum pump, a condenser for the vapour and a receiver for the condensed water. The latter is provided with a sight glass in order to tell when no more water is given off by the material in the oven. The effective working of such a plant depends largely upon the observance of various mechanical and engineering points; the chief feature of the vacuum process is the saving of time that it effects. The oven may be designed to suit either solids or liquids, and provision may also be made for effectively stirring the material during the drying process.

Desiccators. (For an account of laboratory desiccators, *v.* this article, p. 210.)

A desiccator is any type of drying machine, which, working by evaporation, carries the degree of drying to the utmost possible extent. In some of the types previously described, it is difficult to prevent thorough desiccation, and, in fact, to avoid dehydration and calcination, but a number of machines have been devised for the effective desiccation of liquids and thin pastes, which work upon a common principle that may be briefly explained. It consists in spreading the liquid in a thin film over a heated metallic surface kept in motion, and, when the water has been removed, skimming off the solid residue with a knife. By suitable arrangements, this process can be made continuous, and it is employed on a large scale for desiccating milk to a dry powder. A modified method of removing the desiccated product is to cause the liquid to spread out on the upper part of an endless horizontal metallic belt, working over two rollers contained in a heated chamber under reduced pressure. The heated liquid, being fed on to the belt at one roller, is desiccated by the time it arrives at the other, and, on the belt passing over that roller, the dry powder falls into the delivery hopper beneath.

Literature.—Marlow's Drying Machinery and Practice, which contains a bibliography of the subject.

DETONATORS *v.* EXPLOSIVES.

DEXTRAN *v.* GUMS.

DEXTRINS $n(C_6H_{10}O_5)$. When diastase acts on starch paste (gelatinised starch), maltose is the final product, but, intermediate between the starch and maltose, various dextrins are formed as the reaction proceeds in successive stages. These dextrins are colloidal amorphous compounds, and do not form characteristic derivatives. They are soluble in water, and precipitated by alcohol. Only maltodextrin, which is possibly the simplest of them, has been prepared in anything like a state of purity, and most of the other dextrins described must be regarded as mixtures.

As diastatic hydrolysis proceeds, the optical rotatory power diminishes, and the cupric-reducing power increases. The change is rapid to a certain point, but then becomes arrested; this behaviour is interpreted as proof of an essential difference between the higher and lower dextrins. The constants of this stage of hydrolysis are $[\alpha]_J = 162{\cdot}5°$, K (cupric-reducing power) = 48·3, and correspond to the conversion of four-fifths of the starch into maltose. The remaining dextrin is hydrolysed with greater difficulty. According to H. Brown, it cannot have a simpler formula than $40(C_6H_{10}O_5)H_2O$.

The dextrin isolated from a starch conversion stopped at a stage which gives a deep brownish-red colouration with iodine, is termed *erythrodextrin*. At a later stage iodine ceases to give a colouration, and the dextrin present is termed *achrodextrin*. These dextrins have little or no cupric-reducing action, this point being still undecided.

Dextrins are also formed by the action of hot dilute mineral acids, or of heat alone on starch. The final product in this case is dextrose instead of maltose. These methods are used for the commercial preparation of dextrin.

Maltodextrin $6(C_6H_{10}O_5)H_2O$ has $[\alpha]_J + 193{\cdot}6°$, $[\alpha]_D + 181°$; cupric-reducing power, 42. These figures agree with a mixture of 1 part maltose to 2 parts dextrin; but the facts (1) that it cannot be separated into maltose and dextrin by dialysis, (2) that it is not fermentable by yeasts, (3) that it is completely converted into maltose by diastase, prove maltodextrin to be a definite chemical compound. To prepare it, a starch transformation is carried out at 60°–65°, until $[\alpha]_J = +198°$. The solution is boiled, concentrated to a sp.gr. of 1·06, and the maltose removed by fermentation. The solution is filtered, evaporated to a syrup, and digested with alcohol first of 90 p.c., and then of 85 p.c. This last liquid is decanted hot, and the alcohol distilled off, when maltodextrin remains; it is purified by further treatment with alcohol.

On oxidation of maltodextrin with mercuric oxide, until the cupric-reducing power has disappeared, maltodextrinic acid is obtained. This behaviour proves maltodextrin to contain

an aldehyde group, but the change goes further than the oxidation of this group to carboxyl (CO_2H), since it splits up the terminal C_{12} group into a C_5 acid residue, which remains attached to the rest of the molecule, and a C_6 residue which is eliminated.

(For a full account of the decomposition products of starch, *v.* STARCH.)

Manufacture. — The commercial products known as solid dextrin, British gum, starch gum, &c., are mixtures containing various dextrins, together with carbohydrates (copper oxide reducing substances). They consist mainly of erythrodextrin, and accordingly give a brown iodine colouration.

They are prepared (1) by the action of heat on dried starch; (2) by the action of heat on acidified dried starch.

The starch is first freed as much as possible from combined water by drying in suitable ovens, and then submitted to a temperature of 212°–275° in rotating sheet-iron drums. The heat is supplied by hot oil, rape oil being pretty generally used, or by direct fire. When the oil-bath is used, the control over the temperature is greatest, and the colour of the product can be varied at will from white to dark-brown. When the drums are heated by direct fire, they are made to rotate on slightly inclined axes, the dried starch being fed in at the higher end of the revolving cylinder and the product discharged at the other. Sheet-iron ovens are also used; they are constructed singly or in sets. The heat is supplied by a furnace, the heated air from which is drawn over the top of the ovens. The material is kept continually stirred by flat iron oars. Boxes and trays are also used as converters, and, indeed, the maker has only to consider the variety and quality of product required, and to remember that the drier the starch and the lower the temperature of conversion, the whiter will be the product, and, further, that different starches yield different products, *i.e.* behave differently when submitted to the action of heat, to enable him to construct an apparatus that will suit his requirements. It must also be borne in mind that the conversion takes place more slowly at a low temperature.

The alternative method, in which less heat is required to yield a satisfactory product, is to spray or moisten the starch either with a mixture of dilute nitric and hydrochloric acids, or with each acid singly, or with dilute oxalic acid. The paste is dried and heated at 100°–120° or to 150°, till the transformation is complete, as determined by the iodine test; it must then be arrested promptly.

Payen recommended 1000 lbs. starch to be moistened with 30 gallons water containing 2 lbs. nitric acid (sp.gr. 1·38), the mixture to be well kneaded, made up into balls, and dried in a hot-air chamber; then powdered, spread on brass trays to the depth of 1½–2 inches, and submitted to a temperature of from 110°–120° in a hot-air oven.

The products thus obtained appear in commerce in the form of powders varying in colour from almost white to dark-brown, through every shade of light-yellow and brown. They are reduced to this state after roasting, by crushing in pans or passing through rollers, and then sifting through a rotating silk screen such as is used in flour mills.

Dextrins prepared from powdered starch are used by textile manufacturers and calico printers as vehicles for colours. They are also used for all kinds of gum, paste, sizings, and in the manufacture of paper boxes, wall paper, and for a variety of other purposes.

On heating dry starch with formic or acetic acids, the starch nucleus is broken down and esters of dextrins are formed, which are soluble in cold water. The proportion of acid fixed depends on the time of treatment. After 15 hours' heating with glacial acetic acid at 90°, the product just ceases to give a blue iodine colouration, and the products of the further heating are soluble in cold water. When care is taken to exclude moisture, and the heating is continued for 2 or 3 hours only, using equal weights of starch and glacial acetic acid, an acetylated starch, known commercially as *Feculose*, is obtained. This behaves like starch towards boiling water, but the jelly does not revert on standing. It forms very clear flexible films, and is said to give better results than dextrin as a textile finish (*see* Traquair, J. Soc. Chem. Ind. 1909, 28, 288).

Dextrin syrups find employment in a variety of industries. They are prepared from starch by heating it with hydrochloric or sulphuric acids in precisely the manner already described for dextrose (*v.* CARBOHYDRATES), with the exception that conversion is stopped at a much earlier stage. Thus in the modern American process of manufacture of corn syrup from maize starch, less than 10 minutes' heating is required. The product evaporated to 42°–45°B. forms a colourless viscous syrup, having the composition water, 19 p.c.; dextrose, 38·5 p.c.; dextrin, 42·0 p.c.; ash, 0·5 p.c.

In America corn syrup is used extensively in making confectionery, preserves, and table syrups, being preferable to sugar or cane syrup, as the goods are not likely to grain.

Dextrin may also be prepared by the action of malt extract on gelatinised starch.

E. F. A.

DEXTROSE *v.* CARBOHYDRATES.

DHAURA. A gum obtained from *Anogeissus latifolia* (Wall.). It is extensively used in India in calico-printing; it occurs in clean straw-coloured elongated masses, sometimes honey-coloured or even brown from impurities. As an adhesive gum, it is inferior in strength to gum arabic. In India, the reputation of this gum stands high with the calico printers, especially of Lucknow, and it is probable it possesses some specific peculiarity justifying the preference, since it is used with certain dyestuffs, such as with hal li (*Curcuma longa* [Linn.]), whilst gum arabic or 'babul' is used with madder (*Rubia cordifolia* [Linn.]) (Watts' Economic Products of India).

DHURRIN *v.* GLUCOSIDES.

DIABETIN. A trade name for a preparation of lævulose.

DIACETYL *v.* KETONES.

DIACETYLDIOXIME *v.* KETONES.

DIALKYL BARBITURIC ACIDS *v.* PYRIMIDINES.

DIALOGITE. *Manganese carbonate* (*v.* MANGANESE and RHODOCHROSITE).

DIALURIC ACID, *Tartronylurea*

$$CO\begin{matrix}<\\>\end{matrix}\begin{matrix}NH\cdot CO\\NH\cdot CO\end{matrix}>CH\cdot OH$$

prepared by reducing alloxan with zinc and hydrochloric acid, or with sulphuretted hydrogen at the temperature of boiling water (Liebig and Wöhler, Annalen, 26, 276), or with ammonium sulphide, when ammonium dialurate is obtained and is readily converted into the acid by the action of hot dilute hydrochloric acid (Gregory, Chem. Soc. Mem. 1845, ii. 11). A mixture of potassium dialurate and oxalurate is obtained by adding potassium carbonate to a solution of alloxan containing potassium cyanide (Strecker, Annalen, 113, 53); it is prepared by reducing alloxantin with sodium amalgam, or dibromobarbituric acid with sulphuretted hydrogen (Baeyer, Annalen, 127, 12; 130, 133). Magnier de la Source showed that dialuric acid is obtained by prolonged boiling of uric acid with water (Bull. Soc. chim. 1875, 23, 529), and Grimaux effected its synthesis by treating tartronic acid and urea with phosphorus oxychloride (Compt. rend. 1879, 88, 85).

Dialuric acid forms colourless short four-sided prisms, sparingly soluble in cold, more readily so in hot water. The moist crystals or the aqueous solution rapidly absorb oxygen from the air to form alloxan, which combines with the dialuric acid, forming alloxantin. The rate at which the change takes place is illustrated by the results obtained by Hartley (Chem. Soc. Trans. 1905, 87, 1804), in an unsuccessful attempt to obtain the absorption spectra of dialuric acid: 0·144 gram of pure dialuric acid was dissolved by agitation and warming in 100 c.c. of water, and immediately afterwards the solution yielded the same series of absorption spectra as a solution of 0·322 gram of alloxantin, dissolved in 250 c.c. of water. Alloxantin is also formed by mixing solutions of equivalent quantities of dialuric acid and of alloxan. Dialuric acid is monobasic, and, contrary to the statements of Menschutkin (Ber. 1875, 8, 760; Annalen, 1876, 182, 70), forms only one series of salts of the type $C_4H_3O_4N_2M'$. The *sodium*, *potassium*, *ammonium*, and *barium* salts are crystalline (Koech, Annalen, 1901, 315; Behrend and Friederich, Annalen, 1906, 344, 1).

Acetyldialuric acid $CO\begin{matrix}<\\>\end{matrix}\begin{matrix}NH\cdot CO\\NH\cdot CO\end{matrix}>CH\cdot OAc$ crystallises in white prisms or leaflets; m.p. 210°–212°; gives a violet precipitate with barium hydroxide; forms the *potassium salt* $C_6H_5O_5N_2K,H_2O$, and combines with alloxan to form *acetylalloxantin* $C_{10}H_8O_9N_4,H_2O$, m.p. 263°–265°; *benzoyldialuric acid* $C_{11}H_8O_5N_2$, crystallises in prisms, m.p. 209°–210°, yields with barium hydroxide a white precipitate, turning violet, and combines with alloxan to form *benzoylalloxantin* $C_{15}H_{10}O_9N_4,H_2O$ or $1\frac{1}{2}H_2O$, m.p. 253°–255° (Behrend and Friederich, Annalen, 1906, 344, 1–18).

Substituted dialuric acids of the type $CO\begin{matrix}<\\>\end{matrix}\begin{matrix}NH\cdot CO\\NH\cdot CO\end{matrix}>C(OH)R$ are obtained by the condensation of alloxan with (1) aromatic ketones, *e.g.* phenacyldialuric acid, where $R=C_6H_5\cdot CO\cdot CH_2-$; (2) aromatic amines, *e.g.* *p*-aminophenyltartronylurea, where

$$R=NH_2\cdot C_6H_4-;$$

(3) pyrazolone bases, *e.g.* phenylmethylpyrazolonetartronylurea, where $R=\begin{matrix}NPh\cdot CO\\NMe\cdot CMe\end{matrix}\!\!>\!C-$;

(4) phenols, *e.g.* *p*-hydroxyphenyltartronylurea, where $R=OH\cdot C_6H_4-$. For the preparation and technical application of these compounds, *see* art. ALLOXAN.

Dimethyldialuric acid

$$CO\begin{matrix}<\\>\end{matrix}\begin{matrix}NMe\cdot CO\\NMe\cdot CO\end{matrix}>CH\cdot OH$$

obtained by reducing amalic acid (tetramethylalloxantin) with sulphuretted hydrogen (Maly and Andreasch, Monatsh. 1882, 3, 92), or with sodium amalgam (Techow, Ber. 1894, 27, 3082), forms colourless compact crystals which become red at 100° and decompose at 170°. It forms crystalline alkali salts, and reduces cold solutions of silver and copper salts.

***iso*-Dialuric acid**

$$CO\begin{matrix}<\\>\end{matrix}\begin{matrix}NH\cdot CH(OH)\\NH\cdot CO\end{matrix}>C(OH)_2,H_2O$$

or $CO\begin{matrix}<\\>\end{matrix}\begin{matrix}NH\cdot CH(OH)\\NH\cdot CO\end{matrix}>CO,2H_2O$, obtained by the action of bromine water on *iso*-barbituric acid $CO\begin{matrix}<\\>\end{matrix}\begin{matrix}NH\cdot CH\\NH\cdot CO\end{matrix}>C(OH)$ or aminouracil or hydroxyxanthine (Behrend and Roosen, Ber. 1888, 21, 999), crystallises in trimetric prisms sometimes a centimetre long (Weinschenk, Annalen, 1889, 251, 243), is readily soluble in water, less so in alcohol; it loses one molecule of water of crystallisation at 100°. The other molecule, which is regarded as water of constitution, is lost at 140°–150°, at which temperature the compound decomposes. *Iso*dialuric acid is converted into dialuric acid by the action of bases (Koech, Annalen, 1901, 315, 246). It yields uric acid on condensation with urea, reduces solutions of silver salts, and combines with hydroxylamine to form two isomeric *oximino*- compounds. The *α*- oxime forms shining plates or prisms, becomes red and decomposes at 100°; the *β*- oxime crystallises in needles which do not become red at 110° (Behrend and Roosen, Annalen, 251, 244).

Methyl*iso*dialuric acid $C_5H_8O_5N_2$, prepared by oxidising methyl*iso*barbituric acid (Lehmann, Annalen, 1889, 253, 80) with bromine water, crystallises in rosette-like aggregates from water, and in contradistinction to *iso*dialuric acid, contains only 1 molecule of water, which is regarded as water of constitution. M. A. W.

DIAMIDOGEN BLACK, -BLUES *v.* AZO-COLOURING MATTERS.

DIAMINE BETA BLACK, -BLACK, -BLUE, -BRONZE, -BROWNS, -CUTCH, -FAST RED, -GOLD, -GREEN, -PINK, -ROSE, -SCARLET, -VIOLET, -YELLOW *v.* AZO-COLOURING MATTERS; PRIMULINE.

DIAMINES *v.* AMINES.

DIAMINOACRIDYLBENZOIC ACID *v.* ACRIDINE DYESTUFFS.

DIAMINOBENZENES, DIAMINOTOLUENES *v.* AMINES.

DIAMOND. A natural form of carbon, crystallising in the cubic system. The commonest forms are the regular octahedron, the rhombic dodecahedron and the six-faced octahedron, all others being subordinate to these, and occurring

generally in combination with them. The forms are, to some extent, characteristic of the locality: thus the octahedron is common in Cape stones, while Brazil yields rhombic dodecahedra and six-faced octahedra. It is notable that the faces of diamond crystals are often curved, and the six-faced octahedron, with its 48 rounded faces, may become almost a sphere. The curvature is in some cases due to a lamellar structure (*Schalenbildung*), the component lamellæ regularly decreasing in size towards the centre of each face. In a glazier's diamond, it is necessary that the cutting edge be cusped. The faces of diamond crystals are often striated parallel to the edges of the octahedron; they also exhibit impressions, or indentations, frequently of triangular shape, and it is noteworthy that similar impressions may be artificially developed, as shown by G. Rose, by subjecting diamonds to intense heat, without access of air (Ueber das Verhalten d. Diamants u. Graphits bei d. Erhitzung, Monatsb. Berl. Ak. 1872, 516).

The frequent occurrence of triangular depressions on Cape diamonds has been adduced as proof of their exposure to subterranean heat.

Twin crystals of diamond are not uncommon; and flat triangular hemitropes, splitting easily along the plane of union, are known to the Amsterdam workers as *Nahsteine*. (On the crystallisation of diamond, *v.* Sadebeck, Monatsb. Berl. Ak. 1876, 578; Hirschwald, Zeits. f. Krystal. i. 1877, 212; and Weiss, N. Jahrb. f. Min. 1880, ii. 12.)

The cleavage of the diamond is perfect and parallel to the faces of the octahedron. The cutter frequently takes advantage of this cleavage in removing portions disfigured by flaws, and in dressing rough stones to be cut as brilliants. Notwithstanding the ancient belief that a true diamond could bear the blow of a hammer, it is rather a brittle stone, not only splitting along the cleavage planes, but breaking elsewhere with a conchoidal fracture. The hardness of the diamond is indicated as 10 on the mineralogical scale, but it is so greatly superior to that of any other mineral that this is merely an arbitrary expression. Crystals from different localities vary considerably in degree of hardness: thus, lapidaries assert that Indian diamonds are harder than the Brazilian, and these, again, harder than South African stones; whilst those from New South Wales are the hardest of all. The hardness may vary on different faces of a single crystal, and even in different directions on the same face. The sp.gr. of diamond ranges from 3·509 to 3·550, the mean being about 3·514 (Schrötter). Baumhauer determined the density of a nearly colourless Cape diamond to be 3·51812.

Diamonds vary greatly in colour. The purest, or stones of the 'first water,' are practically colourless; while certain stones, known as 'blue whites,' incline to a faint bluish tint; the best example of this type being the Porter-Rhodes diamond—a stone of 150 carats, found at the Cape in 1880. Most of the 'off-coloured' stones present yellow or brown tints; the colour cannot be discharged by heat, but yellow diamonds have sometimes been fraudulently washed with dilute violet ink, whereby the tint is superficially neutralised. The dark colour of some diamonds has been doubtfully referred to the presence of crowds of minute internal cavities, revealed by microscopic examination (Brewster).

Whole off-coloured stones are of comparatively small value, those which possess a pronounced and pleasing colour are highly prized as 'fancy stones.' A deep-red colour is the rarest. The famous 'Hope Blue' diamond of 44½ carats is of a dull slaty-blue; while the 'Dresden Green' diamond, in the Grüne Gewölbe in Dresden, presents a delicate green colour.

The index of refraction is higher in diamond than in any other transparent gem-stone. According to Des Cloizeaux, it is 2·414 for red rays, and 2·428 for green. It was the high refraction of diamond that led Newton to conjecture that it might be 'an unctuous substance coagulated.' The character of the lustre is known as adamantine. Much of the brilliancy of the faceted brilliant is due to its small critical angle (24° 24'), since a very large proportion of the rays entering the diamond must be necessarily returned by total reflection. The coefficient of dispersion is higher than in most transparent bodies; it is given by Jannettaz as 0·044. Examined in polarised light, many diamonds exhibit an anomalous behaviour, apparently due to internal strain. Brewster, who supposed that the diamond might have been originally a vegetable gum, explained the depolarising action which certain diamonds display between crossed nicols as the result of tension caused by included bodies. Chatrian has found a crystal of iron-pyrites in a Brazilian diamond.

After exposure to solar light, the diamond becomes highly phosphorescent, and different faces of the same crystal may emit rays of different colours. Submitted to molecular discharge in Crookes's exhausted tubes, the diamond glows with great brilliancy. On exposure to the heat of the electric arc, it swells up, cracks on the surface, and becomes coated with a substance resembling graphite. In its ordinary state, the diamond does not conduct electricity, but the coke-like mass obtained by exposure to the arc is a good conductor.

The study of the action of heat upon the diamond, with and without the presence of air, gave the earliest clue to its chemical composition. The famous experiment of the Florentine academicians, Averani and Targioni, made in 1694, at the instance of the Grand Duke Cosmo III., showed that it could be volatilised by heat. In 1751 the Emperor Francis I. caused a quantity of diamonds and rubies to be placed in a crucible and exposed to great heat, when it was found that the diamonds disappeared, while the rubies were fixed. Darcet afterwards showed that, though the diamonds vanished if heated in an open crucible, they remained unaltered if air were completely excluded. In 1772 Lavoisier demonstrated that the diamond is truly combustible, and yields carbon dioxide; and it was subsequently shown by Smithson Tennant that equal weights of charcoal and of diamond gave equal weights of this gas. By heating diamond with iron, Guyton de Morveau obtained steel, and thus indirectly showed the probable composition of the mineral. The experiments of Davy, in 1816, proved that the diamond was practically pure carbon: a result confirmed by

the refined investigations in determining the atomic weight of carbon by Dumas and Stas, and subsequently by Roscoe and by Friedel. The behaviour of diamonds when exposed to high temperatures in various gaseous media has been studied by M. Morren (Compt. rend. 70, 990).

On the combustion of the diamond, there remains a quantity of a colourless or reddish ash, varying from one five-hundredth to one two-thousandth of the original weight of the mineral. Microscopic examination of this delicate spongy ash led Göppert, Petzholdt, and others to believe that it shows traces of cellular tissue, suggestive of a vegetable origin.

Various hypotheses have been advanced to explain the origin of the diamond, but these have rarely been subjected to experimental verification or disproof. Liebig suggested the decomposition of liquid hydrocarbons, while Chancourtois and others have resorted to hydrocarbonaceous vapours. Carvill Lewis, basing his opinion on the occurrence of diamonds in South Africa, derived the mineral from the action of eruptive rocks on carbonaceous shales (Geol. Mag. 1887, 22). As many of the minerals associated with the diamond in Brazil have been formed artificially by the decomposition of chlorides at a high temperature, it has been suggested by A. Favre that the decomposition of chloride of carbon may have yielded the diamond. Gannal attempted to obtain it from carbon disulphide. Reviewing the geological conditions under which diamonds occur in various parts of the world, it is seen that these are so different in different localities as to suggest that the natural process of diamond-making has not been uniform. Thus, in Brazil and in India the diamond appears to be associated with acid rocks, while in South Africa it occurs in a highly basic rock, resembling an altered peridotite.

The artificial production of diamond, though many times attempted with doubtful results, was successfully accomplished by H. Moissan, in 1893, by the crystallisation of carbon from its solution in iron at a high temperature and under enormous pressure. This was effected by plunging molten iron from an electric furnace into cold water; the contracting crust so formed holding the molten interior under pressure. The largest crystal of diamond so obtained measured ½ mm. across. Microscopic crystals have also been obtained by I. Friedländer (Geol. Mag. 1898, 226) and by R. v. Hasslinger (S. B. Ak. Wien, 1902, 111, ii. *b*, 619; 1903, 112, ii. *b*, 507), by dissolving carbon in molten olivine.

The most ancient diamond-mines are those of India, whence the precious stone has been obtained from remote antiquity. The Indian diamonds are found in river gravels, and in superficial deposits scattered over the country, while occasionally they occur in sandstones of the Vindhyan formation, but these probably do not represent the original matrix. In 1884 Chaper announced the discovery of the diamond in a pink pegmatite, at Bellary in Madras (Compt. rend. 1884, 98, 113), but this seems doubtful. Diamonds have been worked in three extensive districts in India. The mines of the most southern group are partly in the Madras Presidency and partly in the territory of the Nizam, the most famous workings having been those on the Kistna and Godavery rivers, improperly known as the mines of Golconda. The 'Golconda' district yielded most of the great historical diamonds, such as the Koh-i-nur, the Regent, and the Great Mogul; and workings have been reopened at Partial (W. Morgans' Report, 1889). Diamonds also occur in the districts of Cuddapah, Bellary, and Karnul, but most of the mines are now abandoned. In 1881 a diamond of irregular shape, weighing 67⅞ carats, was found near Wajra Karur, in the Bellary district, and yielded a fine brilliant of 24½ carats, known as the 'Gor-do-Norr' (Mallet). Another group of diamond localities is situated in the Central Provinces: at Sambalpur on the Mahanadi river, and at Wairagarh. The mineral is also found in Chutia Nagpur in Bengal; while further to the north is a third group of mines, including those of Panna in Bundelkhand, still worked on a limited scale. (On Indian diamonds, *v.* Manual of the Geol. of India; vol. 3, Economic Geology, by V. Ball, 1881; and vol. 4, Mineralogy, by F. R. Mallet, 1887.)

Although the sands of many of the rivers of Brazil had been long worked for gold, it was not until 1727 that the occurrence of diamonds in association with the precious metal was observed. The distribution of the diamond is extensive, occurring locally in the states of Minas Geraes, Goyaz, Bahia, Matto Grosso, Parana, and São Paulo. The best-known locality is Diamantina, formerly callel Tejuco, in Minas Geraes. The diamond occurs in gravels mixed with clay, and forming a loose conglomerate known as *cascalho*; while if the quartz pebbles are less rolled, as in the plateau gravels, it is termed *gurgulho*. The diamond is said to have been found in a metamorphic sandstone called *itacolumite*, and it is asserted that where itacolumite is not present the neighbouring gravels never bear diamonds. In the Diamantina region, the original matrix seems to be in veins of quartz and clayey matter, carrying iron-pyrites and tourmaline, and traversing a series of hydromica-schists and itabarites, with itacolumite. In the sands and gravels, the diamond is associated with rutile, anatase, brookite, magnetite, hematite, ilmenite, &c. (On Brazilian diamonds, *v.* papers by Orville Derby in Amer. J. Sci. [3] 24, 1882, 34; and Gorceix in Compt. rend. 113, 1881, 981; H. Pearson, J. Soc. Arts, 58, 1909, 101.)

It appears that the occurrence of diamonds in South Africa was known as far back as the middle of the 18th century, yet it was not until 1867 that attention was recalled to this forgotten discovery. At that time, the child of a Boer farmer near Hopetown, picked up among the pebbles of the Orange river a diamond weighing 21 3/16 carats. Search in the neighbourhood soon led to other discoveries, one of the earliest being that of a stone of 83½ carats, which came to be known, when cut, as the 'Star of South Africa,' or the 'Dudley' diamond. The earliest workings were 'river diggings,' in the gravels of the Vaal and some of its tributaries, especially near Pneil and Klipdrift. The largest diamond obtained from the river diggings was the 'Stewart,' a stone weighing 288⅜ carats, found in 1872 at Waldeck's Plant, on the Vaal. On the discovery of diamonds in the soil at Du

Toit's Pan, most of the river diggings were abandoned in favour of what were called 'dry diggings.' The principal mines at present worked are those of Kimberley, De Beer's, Du Toit's Pan, Wesselton, and Bultfontein, all within a limited area around the town of Kimberley in Griqualand West. There are also several smaller isolated mines in Griqualand West and in Orange River Colony, in the latter notably the Jagersfontein and Koffyfontein mines. The largest pipe of 'blue ground' is that of the Premier mine, near Pretoria in the Transvaal, which was discovered in 1903; here, in 1905, was found the largest by far of known diamonds, the 'Cullinan,' which weighed in the rough 3025¾ English carats (=621·2 grams).

The South African diamonds occur mostly in a serpentinous breccia, filling vertical pipes, which, piercing the surrounding rocks, rise to the surface, where their presence was originally marked by little hills or *kopjes*. A reddish sandy soil occupied the surface, beneath which occurred a deposit of calcareous tufa; this passed downwards into the 'yellow earth,' which finally merged into the so-called 'blue ground.' The yellowish material was simply the upper part of the blue earth more or less altered by surface agencies.

It is now generally believed that the pipes, or chimneys, are ancient volcanic ducts, through which the diamond-bearing material has been brought up from some deep-seated source. The pipes traverse black and reddish shales of the Karoo formation, believed to be of Triassic age, associated with sheets of basaltic rocks, and resting upon a granite base. The edges of the shales are slightly upturned, as if by pressure from below, but they do not show signs of fusion or other alteration suggestive of a high temperature. The walls of the chimneys are smooth, or vertically striated, and between the walls and the contents of the pipes there are occasional hollows lined with crystals of calcite, and sometimes yielding explosive gases, apparently derived from the carbonaceous shales.

The materials filling the pipes consist of fragments of the shales and other neighbouring rocks, usually sharp at the edges and not fused, cemented into a hard breccia by a greenish serpentinous material, chiefly a hydrated ferromagnesian silicate, which is probably an altered enstatite or bronzite (for analysis, *v.* Maskelyne and Flight, Quart. Journ. Geol. Soc. 30, 1874, 406). The embedded diamonds are associated with garnets (pyrope), sometimes known in the trade as 'Cape rubies'; with green salite, and a peculiar mica, named by Maskelyne *Vaalite*, which appears to be an altered biotite. Ilmenite is present, and is sometimes mistaken for carbonado or black diamond. Among the other associates of the diamond are iron-pyrites, magnetite, and zircon. It is notable that the diamonds are often fragmentary, and neighbouring fragments do not correspond, thus suggesting that fracture occurred at some deep-seated point. Much discussion has arisen as to the original character of the blue rock; but most geologists now regard it as an altered volcanic product which was probably brought up in a pasty condition, not at a very high temperature, but perhaps rather like the materials of a mud volcano. Carvill Lewis described the rock as an altered peridotite under the name of *Kimberlite*, and concluded that the matrix of the diamond in many parts of the world was probably serpentine, resulting from the alteration of an erupted peridotite (Rep. Brit. Ass. 1887 meeting, 720).

Until 1885 the diamond-mines of South Africa were worked as open quarries; but, serious difficulty having arisen from falls of the surrounding rock, known locally as 'reef,' systematic underground mining has been introduced. Outside the pipe a shaft is sunk, and galleries are thence driven into the diamond ground. The blue earth, when first hauled up, is extremely hard, but by exposure to air and water it is readily disintegrated, and the diamonds are then separated by washing. (For account of the South African diamond-mines, *v.* G. F. Williams, The Diamond Mines of South Africa, 1902, new ed. 1906; P. A. Wagner, Die Diamantführenden Gesteine Südafrikas, 1909.)

More recently, diamonds have been found in other parts of South Africa, namely, in Southern Rhodesia and in German South-West Africa. In the latter region, large numbers of small diamonds were discovered in 1908 in the sand-dunes of Lüderitz Bay.

Borneo has yielded diamonds from remote antiquity. They occur in alluvial clays, river sands, and drift gravels; occasionally, too, they have been found in an Eocene conglomerate, but this is a derived rock, and the original matrix is unknown (*v.* Posewitz's Borneo, Berlin, 1889).

In Australia, diamonds are known to occur at numerous localities, especially in New South Wales, but the stones are invariably small. They have been worked commercially in drift gravels on the Cudgegong river, near Mudgee, and at Bingera and Inverell in New South Wales (*v.* Liversidge, Min. of New South Wales, 1888, 116). Diamonds have also been found, though but rarely, near Echunga in South Australia, and at Beechworth and elsewhere in Victoria.

Numerous localities for diamonds are known in the United States. They occur in association with gold in North Carolina, in Georgia, and in Butte Co., California; while they are found with platinum in Oregon. A crystal weighing 23¾ carats was found in 1855 at Manchester in Virginia, and after cutting became known as the On-i-nur, or 'Sun of light.' (On diamonds in United States, *v.* G. F. Kunz, in successive volumes of Mineral Resources, by United States Geolog. Survey.)

Other localities for diamonds are in British Guiana, where stones were first met with in 1890 in the upper courses of the Mazaruni river. The only European localities are in the Ural Mountains, where a few isolated crystals have been found in the gold washings at different times since 1829, and in Lapland.

It has lately been shown that the diamond is to be included in the list of extra-telluric minerals. Microscopic crystals of carbonado have been detected in the meteoric stones which fell at Novo-Urei in Russia on September 22, 1886, and also in the meteoric irons of Cañon Diablo in Arizona.

Carbonado is the name given to a black or dark-grey form of diamond, which was discovered in 1842 in the state of Bahia in Brazil, and is at present known to occur only in Brazil

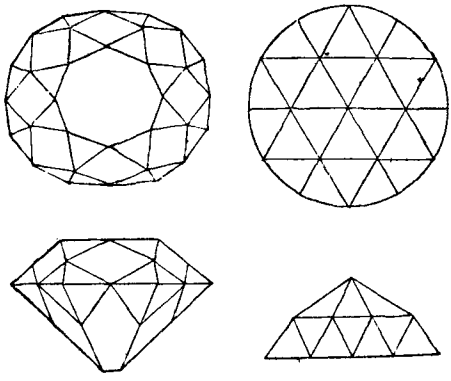
and Borneo. It is generally found in irregular or rounded masses, occasionally with indistinct crystalline form, and presenting on fracture a compact granular or cellular structure. Its sp.gr. is less than that of true diamond, being in some cases as low as 3·01; nor is it so pure as crystallised diamond, some specimens yielding on combustion as much as 2 p.c. of ash. Notwithstanding its impurity, it exceeds in toughness any other form of diamond; and this has led to its extensive use in the arts. In the diamond-mounted rock-drills of Leschot, and Beaumont, pieces of carbonado are firmly embedded in the inner and outer edges of the steel tube which forms the head of the drill; and so valuable is the carbonado that a single crown, with its setting, may be worth 2000*l*. The carbonado is also used in tools for dressing millstones and emery wheels.

Another variety of diamond used in the arts is known as *bort* or *boart*. Mineralogists recognise under this name an impure translucent and imperfectly crystallised variety, generally occurring in small concretionary masses of dark-grey or black colour, with a rugose exterior. It is slightly less dense than crystallised diamond, its sp.gr. not exceeding 3·505; but it is extremely hard. True bort occurs in most diamond-bearing districts, but much of the bort of commerce is merely coarse diamond, too much flawed or splintered to be used by the jeweller, The bort is crushed in a steel mortar, and the powder is extensively employed by lapidaries and others as a powerful abrading agent.

The art of cutting and polishing the diamond is generally attributed to Ludwig van Berquen, of Bruges, who is said to have first practised it about 1476. The forms into which diamonds are cut at the present day are known as the *brilliant* and the *rose* or rosette. The former may be roughly described as consisting of two truncated and faceted pyramids, applied base to base: the upper part, or *crown*, is more truncated than the lower part; the edge of union between the two parts is termed the *girdle*, while the broad flat upper face is the *table*, and the small lower plane the *culet*. The rose has a flat base, from which rises a hemispherical dome covered with triangular facets (*v.* figs.).

In cutting a diamond, the first step is usually to reduce it by cleavage to a convenient shape. To cleave the crystal, the operator embeds it in a cement of resin and brickdust, carried at the end of a small wooden bâton. The cement having been warmed, the diamond is fixed in such a position that only the part to be split is exposed. Along the direction of cleavage a furrow is cut by means of another diamond; into this groove a thin steel blade is inserted, and by a sharp blow, skilfully delivered on the blade, the cleavage is effected.

After cleavage, the stone is cut, or rather rubbed, into the required shape. Two diamonds, each embedded in cement, with only a small surface exposed, are patiently rubbed together until, by mutual attrition, two approximately plane surfaces are formed. The operator wears stout gloves to protect the fingers, and takes care that every particle of dust resulting from the friction is carefully preserved. When the faces have been roughly formed by this rubbing, or 'bruting,' they require to be polished on the mill. The diamond is embedded in a ball of fusible metal, carried in a hemispherical cup at the end of an arm, which being loaded with movable weights enables the manipulator to adjust the pressure on the wheel. The wheel is a circular iron disc, about 10 inches in diameter, rotating in a horizontal plane at the rate of about 2000 or 3000 revolutions per minute. The rotating discs are fed with diamond-dust and olive oil.



Brilliant-cut. Rose-cut.

The diamond-cutting industry has for centuries been centred in Amsterdam, where it is mainly in the hands of Jews; but mills have also been established at Antwerp, and, of late years, at Hanau, near Frankfort; in Switzerland, London, and New York. The trade has received a great impetus in recent years by the enormous output of the South African mines, which now practically supply the world.

For information on the diamond, *v.* M. Bauer, Edelsteinkunde, 1896, 2nd ed. 1909; Engl. transl. by L. J. Spencer, 1904; G. F. Williams, The Diamond Mines of South Africa, 1902, new ed. 1906; Sir W. Crookes, Diamonds, 1909; Annual Reports on Precious Stones by G. F. Kunz (in The Mineral Industry) and by D. B. Sterrett (in Min. Res., United States).

L. J. S.

DIAMOND BLACKS, -FLAVINE, -GREEN, -YELLOWS *v.* AZO- COLOURING MATTERS.

DIANA. The alchemistic name for silver.

DIANIL BLACK, -BLUE, -PONCEAU, -YELLOWS *v.* AZO- COLOURING MATTERS; PRIMULINE.

***o*-DIANISIDINE** *v.* DIPHENYL.

DIANISIDINE BLUE *v.* AZO- COLOURING MATTERS.

DIANOL BRILLIANT RED, -RED *v.* AZO- COLOURING MATTERS.

DIANTHINE *v.* AZO- COLOURING MATTERS.

DIAPHTHERIN, DIAPHTHOL, DIASPIRIN, *v.* SYNTHETIC DRUGS.

DIASPORE, *Native hydrated alumina* Al_2O_3, H_2O (*v.* ALUMINIUM).

DIASTASE or *Amylase* is the name given to the enzyme or mixture of enzymes which converts starch and glycogen into maltose. In France, the word 'diastase' is used as a general term for all enzymes, a custom which caus-es

considerable confusion, and which it is to be hoped will lapse.

Diastase is very widely distributed in plants and in animals. It is found in blood serum, in muscle, liver and pancreas, and particularly in the saliva, this latter enzyme being long known under the name *ptyalin*.

The power of germinated barley to hydrolyse starch was discovered by Kirchoff in 1814, and the enzyme preparation was first made by Payen and Persoz in 1833. Diastase is found very generally in the leaves and twigs, in the germinating seeds, in the bark, in the pollen grains, and in the latex of plants. It occurs in yeast and in most of the mould fungi, the enzyme of *Aspergillus oryzæ*, the so-called *Taka diastase* being well known on account of its industrial use in the manufacture of the Japanese beverage, koji.

Diastase, like all other enzymes, has not been prepared in anything approaching a pure state. Considerable uncertainty exists also as to whether it is a single enzyme or a mixture of enzymes acting in turn to convert starch into dextrin and dextrin into maltose. Modern evidence favours the view that it consists of a starch-liquefying enzyme or *amylopectase*, and a saccharifying enzyme able to hydrolyse soluble starch, but without much action on raw starch until this has been rendered soluble by the amylopectase. The two enzymes are found together, but in unequal proportions. Wheaten flour, for example, frequently has a deficiency of liquefying enzyme.

There are well-marked differences between the enzymes present in resting barley and in malt (*cf.* Lintner and Eckhardt, Zeitsch. Ges. Brauw. 1899, 389; J. L. Baker, Chem. Soc. Trans. 1902, 81, 1177), one of the chief of these being that the diastase of raw grain possesses little if any starch-liquefying power. Baker has shown that the products of hydrolysis of starch by alcohol-precipitated enzymes from the two sources, are not the same. Brown and Morris have termed the enzyme of resting barley 'translocation diastase,' that of malt 'secretion diastase' (Chem. Soc. Trans. 1890, 58, 458; 1893, 63, 604). They regarded these as not only different in their actions, but as formed from different materials. This latter assumption has been disputed (*cf.* Ling, J. Inst. Brewing, 1908, 14, 494; Ford and Guthrie, *l.c.*, 1908, 14, 61).

Some authors consider the saccharifying enzyme to be a mixture, attributing a different enzyme to each stage in the simplification of the starch molecule. It is impossible at present to make any definite statement on this point. In support of it, it appears that exposure to a temperature of 68° acts more injuriously on the conversion of dextrin to maltose than on that of starch into dextrin. Heating diastase does not affect the liquefying power, though the saccharifying action largely disappears.

The quantity of diastase contained in the barley grain increases gradually in the course of germination: it is said to reach a maximum in about 8 or 9 days, when the plumules are twice as long as the grains.

Preparation.—A great variety of methods have been proposed for the preparation of diastase, the majority of these starting from malt. According to O'Sullivan (Chem. Soc. Trans. 1884, 45, 2), finely ground pale barley malt is saturated with water, adding enough to slightly cover it and after 3–4 hours as much of the solution as possible is expressed by means of a filter press. After filtering, alcohol (sp.gr. 0·83) is added, as long as a flocculent precipitate forms, the addition being discontinued as soon as the liquid becomes opalescent or milky. The precipitate is collected, washed with alcohol of increasing strength until dehydrated, pressed between cloth and dried *in vacuó* over sulphuric acid.

Lintner (J. pr. Chem. 34, 378) treats 1 part of green barley malt or flour of air-dried malt with 2 to 4 parts of 20 p.c. alcohol for 24 hours, and precipitates the extract with 2½ volumes of absolute alcohol. The precipitate is washed with alcohol and ether to dehydrate it, and dried *in vacuó*.

Loew extracts germinated barley with 4 p.c. alcohol, and precipitates the extract with basic lead acetate. The precipitate is suspended in water, lead removed with hydrogen sulphide, and the enzyme precipitated with a mixture of alcohol and ether.

Wroblewsky extracts finely powdered malt, first with 70 p.c. and then twice with 45 p.c. alcohol. Alcohol is added to the two last extracts until 70 p.c. is present, the precipitate formed is collected, washed with alcohol and ether, and dried.

For further purification, both Wroblewsky and Osborne and Campbell dissolve the enzyme in water, and precipitate it with ammonium sulphate, which is added, drop by drop, until the liquid contains 50 p.c. On standing, a very active yellowish flaky precipitate is obtained.

Green barley malt may also be extracted with glycerol, and the diastase precipitated by alcohol. Effront extracts with water and induces alcoholic fermentation in the extract so as to remove carbohydrate and protein matter. It is then filtered and the diastase precipitated by alcohol.

Animal diastase is best obtained from saliva. Cohnheim uses freshly prepared calcium phosphate as precipitant, extracts this precipitate with water, and adds alcohol to obtain the enzyme. Alcohol is also used for direct precipitation, likewise ammonium sulphate. Von Wittich extracts pancreas diastase with glycerol.

For the preparation of an active diastatic extract for laboratory use, ground malt should be extracted with twenty times its weight of distilled water at 21° for 3 hours and filtered bright.

Preparations of diastase obtained as described above are colourless, amorphous, and friable, readily dissolving in water; but if allowed to dry without being dehydrated, they are horny and not easily penetrated by water. They invariably contain ash, which consists of potassium, calcium, and magnesium phosphates, with a trace of sulphate. They give a deep blue colour with a 1 p.c. alcoholic solution of gum guaiacum and hydrogen peroxide.

Lintner's diastase gave the reactions of the proteins, and was found to contain C, 46·66 p.c.; H, 7·35 p.c.; N, 10·42 p.c.; S, 1·12 p.c., calculated on the ash-free product. Osborne (Ber. 1898, 31, 254) found for his most active preparation, which had a diastatic power of 600 and

contained 0·66 p.c. of ash, C=52·5 p.c., H =6·72 p.c., N=16·1 p.c., S=1·9 p.c.; and Wroblewsky gives N=16·5 p.c. for his purest diastase. Both authors regarded diastase as a protein combined, according to Osborne, with a proteose.

The most recent work of Frankel and Hamburg (Beitr. Chem. Physiol. n. Path, 1906, 8, 389) leads to the conclusion that diastase contains neither protein groups nor reducing carbohydrates in its molecule. Impurities were removed from the enzyme solution with lead acetate, the solution sterilised by filtration, and further purified by fermentation with a yeast which had been rendered nitrogen-hungry. This preparation could be divided by dialysis into two distinct enzymes, one of which—the saccharifying—passed through the paper, while the other—the liquefying—was left behind. It showed absence of typical protein reactions, but contained a pentose in small amount.

The activity of diastase is very greatly influenced by the nature of the substrate on which it acts, more particularly as to whether this is alkaline or acid. Certain substances, such as the amphoteric amino- acids and asparagine, also ammonium and calcium phosphate, increase the activity, asparagine being especially effective in some instances. Vegetable diastase exhibits the maximum activity in presence of traces of weak organic acids. The very smallest quantities of alkali stop action, though this begins again as soon as the alkali is neutralised. In reality, the above accelerating substances are all of acid nature, and the apparently favourable effect of acid is due not to the acid *per se*, but to its neutralising alkaline impurities present. Maximum activity is attained in neutral (in the sense that water is neutral) solution. Minute traces of metallic impurities have an adverse influence. The temperature of maximum activity of diastase is about 55°; heated above this, it begins to show decomposition.

Estimation of diastatic power.—Since it has not been obtained in a pure state, the absolute estimation of diastase is an impossibility; moreover, the very great influence of external conditions on diastatic activity, to which allusion has been already made, makes it difficult to do more than compare the relative activities of a number of materials under precisely similar conditions. As this is an important operation in brewery control, the methods of analysis have been accurately laid down. The diastatic power is often termed the Lintner value, and expressed in degrees Lintner. The standard is 100° when 0·1 c.c. of a 5 p.c. solution of malt, acting on a 2 p.c. solution of soluble starch for 1 hour at 70°F., produces reducing sugar equivalent to 5 c.c. of Fehling's solution.

To obtain accurate results, great stress must be laid on the purity of the distilled water and soluble starch used: commercial starches are frequently alkaline. All work must be carried out in hard-glass apparatus (*cf.* Ford, J. Soc. Chem. Ind. 1904, 23, 8).

The method adopted by the Malt Analysis Committee of the Institute of Brewing (J. Inst. Brewing, 1906) for malt, is as follows: 25 grams ground malt are extracted with 500 c.c. of distilled water for 30 hours at 70°F. and filtered bright. 3 c.c. is allowed to act on 100 c.c. of 2 p.c. soluble starch at 70° F. for 1 hour. Diastatic action is then stopped by the addition of 10 c.c. *N*/10-sodium hydroxide, and the liquid made up to 200 c.c. Sugar is then determined either volumetrically or gravimetrically. The results are calculated by the formula

$$\text{Diastatic power} = 1000/xy$$

where x = the number of c.c. of malt extract contained in 100 c.c. of the fully diluted starch-conversion liquid, and y = the number of c.c. of the same liquid required to reduce 5 c.c. of Fehling's solution. When the diastatic capacity exceeds 50°, 2 c.c. or less of malt extract are taken, particularly for the malts over 80° used by distillers and vinegar makers. The diastatic power of English brewing malt ranges between 35° and 40°, that of green malt from 110°–125°, showing that a large proportion of the enzyme is destroyed during the kilning.

Lintner tests solid preparations of the purified enzyme by dissolving 0·2 to 0·5 gram in 50 c.c. water and adding to a series of test-tubes, each containing 10 c.c. of 2 p.c. soluble starch solution, 0·1, 0·2, &c., up to 1 c.c. of the enzyme solution. After an hour, each tube is boiled in the water-bath with 5 c.c. of Fehling's solution, and that determined in which the copper solution is just completely reduced. A second series enables this point to be ascertained with greater accuracy.

Similar methods have been based on the colourations with iodine, shown by starch and dextrin solutions. Wohlgemuth sets increasing quantities of enzyme in a series of tubes with 5 c.c. of a 1 p.c. starch solution under precisely similar conditions. After 30 to 60 minutes at 40°, the tubes are cooled in ice and a drop of *N*/10 iodine solution added. Colours varying from dark-blue, blue-violet, reddish-yellow, and yellow are obtained. Wohlgemuth selects the tube in which the violet shows as indicating complete conversion to dextrin.

Uses.—Diastase plays a most important part in the brewing, distilling, and baking industries. Malt extracts, concentrated *in vacuó* at a low temperature to viscid syrups, are largely used by bread bakers and in some food preparations. Considerable quantities of such active preparations, made from malts of high diastatic power, also find employment in laundries for the purpose of removing starch from stiff collars, shirts, &c. (*See also* articles STARCH; FERMENTATION; HYDROLYSIS.) E. F. A.

DIATOMACEOUS EARTHS, DIATOMITE *v.* KIESELGUHR.

DIAZINE BLACK, -BLUE, -GREEN *v.* AZO-COLOURING MATTERS.

DIAZO- COMPOUNDS. These organic substances, like the azo- compounds, contain the characteristic group $-N_2-$, but whereas, in the latter series, this bivalent radicle is invariably attached to two carbon atoms, $C{\cdot}N_2{\cdot}C$, in the former it is generally, although not invariably, combined with only one carbon atom, the other valency being satisfied by (1) an electro-negative ion $\bar{A}c$ in the *diazonium salts* $C{\cdot}N_2{\cdot}\bar{A}c$; (2) an oxygen atom in the *diazohydroxides* ('*diazohydrates*') $C{\cdot}N_2{\cdot}OH$ and *diazo-oxides* ('*diazo-*

tates') $C{\cdot}N_2{\cdot}OR$; (3) a nitrogen atom in *diazoamines* (*diazoamino- compounds*)

$$C{\cdot}N_2{\cdot}NHR$$

and *diazoimines* (*azimino- compounds*)

$$C{\cdot}N_2{\cdot}NH{\cdot}C:$$

(4) a sulphur atom in *diazosulphonates*

$$C{\cdot}N_2{\cdot}SO_3K$$

and *diazosulphides* $C{\cdot}N_2{\cdot}S{\cdot}C$.

The *diazocyanides* $C{\cdot}N_2{\cdot}CN$ contain the azo-group attached to two carbon atoms, one of which belongs to a cyanogen group, and these compounds which, in general, are distinctly coloured, form an intermediate group between the foregoing diazo- derivatives and the azo- compounds.

Certain aliphatic diazo- compounds (*v. infra*) contain the group $-N_2-$ attached by both its active valencies to the same carbon atom.

I. Diazonium Salts.

These diazo- derivatives are generally, but not exclusively, prepared from aromatic amines, and the process, which is termed *diazotisation*, is carried out with the undissociated salt of the amine, and not with the free base. In a hydrolysing solvent like water, it is therefore customary to diazotise aniline and its derivatives with sodium nitrite (1 molecule) and excess (2½ to 3 equivalents) of mineral acid.

Aromatic Diazonium Salts.

The diazotisation of the benzenoid and naphthalenoid amines is frequently carried out on a manufacturing scale owing to the employment of aromatic diazonium salts in the production of azo- colouring matters. More than 1000 tons of para-nitraniline are diazotised annually in the production of 'para-nitraniline red.'

The aromatic base is dissolved in dilute hydrochloric or sulphuric acid (3 equivalents in 10-20 p.c. aqueous solution) and the solution treated with an equivalent quantity (1 molecule) of sodium nitrite in 10-20 p.c. solution. The diazotisation is completed when the liquid contains a slight excess of nitrous acid as indicated by starch and iodide paper.

With aniline and its homologues, the temperature of the diazo- solution is generally maintained at 0°-5° to prevent, so far as possible, the decomposition of the unstable diazonium salt, but in other cases, *e.g.* the nitranilines, naphthylamines, benzidine, and other diphenyl bases, the diazotisation is carried out most readily at 10°.

In the manufacture of soluble azo- dyes, the diazonium salts are generally employed in aqueous solution, but solid diazo- compounds, in dry or paste form, have been introduced to enable dyers to prepare 'ingrain' azo- colours which are developed on the textile fibres (*v.* Eng. Pat. 18429, 21227, 1894; 8989, 11757, 1895; 1645, 1896; 15353, 1897; D. R. PP. 85387, 88949, 94280, 1894; 89437, 1896).

In alcoholic or acetic acid solution, diazotisation can be effected on the salt of the amine without using an excess of acid, and ethyl or amyl nitrite may, with advantage, be substituted for sodium nitrite.

Benzenediazonium chloride $C_6H_5{\cdot}N_2Cl$, the simplest example of an aromatic diazonium salt, is prepared by adding the calculated quantity of amyl nitrite to aniline hydrochloride suspended in glacial acetic acid at 10°; it is precipitated from the clear solution thus obtained by the addition of ether.

Benzenediazonium sulphate $C_6H_5{\cdot}N_2{\cdot}HSO_4$ is prepared in a similar manner from aniline sulphate suspended in glacial acetic acid, the precipitation being effected with alcohol and ether.

Benzenediazonium nitrate $C_6H_5{\cdot}N_2{\cdot}NO_3$, which was first precipitated from aqueous solution by ether and alcohol (Griess, Annalen, 1866, 137, 39), can also be produced in alcoholic or glacial acetic acid solution (Knoevenagel, Ber. 1890, 23, 2995; Bamberger, *ibid.* 1896, 29, 446; Hirsch, *ibid.* 1897, 30, 92; Hantzsch and Jochem, *ibid.* 1901, 34, 3337).

Diazonium salts have been obtained with a large variety of anions: *platinichlorides, aurichlorides, stannichlorides, ferricyanides, nitroprussiates* (Ber. 1879, 12, 2119; 1885, 18, 965), *chromates* (Jahresberichte, 1867, 915; Chem. Soc. Trans. 1905, 87, 1), *carbonates* and *nitrites* (*ibid.* 1905, 87, 921), *fluorides* (Ber. 1903, 36, 2059), *perchlorates* (*ibid.* 1906, 39, 2713, 3146), *picrates* (Chem. Soc. Trans. 1907, 91, 1316), *azides* (*ibid.* 1910, 97, 1697; Ber. 1903, 36, 2056).

All diazonium salts are liable to explode in the dry state, for they are endothermic compounds (Berthelot and Vielle, Compt. rend. 1881, 92, 1076; Sventoslavsky, Ber. 1910, 43, 1479) and in some cases the explosion point has been determined (Ber. 1899, 32, 1691; 1900, 33, 527). The diazonium chromates and perchlorates decompose with considerable violence, so that the former have been suggested as explosives (Bull. Soc. chim. 1867, [2] 7, 270; Fr. Pat. 73286).

Bisdiazonium salts (*Tetrazo- salts*). These compounds are produced from aromatic diamines which do not contain their amino-groups in *ortho-* or *peri-* positions (*v. Cyclic diazo- compounds*, p. 230).

When the two amino- groups are in the same aromatic nucleus, complete diazotisation is effected only with some difficulty. Metaphenylenediamine hydrochloride and sodium nitrite furnish the azo- colouring matters included under the term 'Bismarck brown' (Ber. 1897, 30, 2111, 2899; 1900, 33, 2116), but when a solution of the base in excess of hydrochloric acid is added quickly to a large excess of well-cooled aqueous nitrous acid, complete diazotisation takes place and *benzene-m-bisdiazonium chloride* $C_6H_4[N_2{\cdot}Cl]_2$ is produced. Para-phenylenediamine hydrochloride, when diazotised in the usual way, gives a mixture of diazonium and bisdiazonium chlorides, but when the hydrochloride is added to excess of nitrous acid, *benzene-p-bisdiazonium chloride* is obtained.

In the naphthalene series, 1:4-naphthylenediamine is diazotised with difficulty, owing to its oxidisability, but in producing its azo- derivatives, this difficulty is surmounted by working with its monoacyl- derivatives and diazotising in two stages with an intervening hydrolysis (Eng. Pat. 18783, 1891). The heteronuclear naphthylenediamines, excepting the 1:8- compound, can be completely diazotised, yielding *naphthalenebi-diazonium salts* (Ewer and Pick, D. R. PP. 45549, 45788; Badische Anilin und Soda Fabrik. D. R. P. 130175; Morgan and

Micklethwait, Chem. Soc. Trans. 1910, 97, 2558). Benzidine, tolidine, dianisidine, and other similar heteronuclear diamines of the diphenyl and ditolyl series are readily diazotised, furnishing bisdiazonium salts (*e.g. diphenylbisdiazonium chloride* $Cl{\cdot}N_2{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}N_2{\cdot}Cl$), which are employed in the manufacture of substantive azo-dyes (*v. Congo red* and *Benzopurpurin*; art. AZO- COLOURING MATTERS). There are certain substituted para-diamines in both benzene and naphthalene series which have hitherto resisted all attempts at complete diazotisation (Ber. 1884, 17, 603; 1896, 29, 2285; Eng. Pat. 2946 of 1896).

VELOCITY OF DIAZOTISATION.

Under the usual experimental conditions, diazotisation proceeds with great rapidity, but in N/1000 solutions, the velocity of this reaction has been determined by a colorimetric method for estimating the free nitrous acid. The reaction is of the second order, and the values of the constant $C=\frac{x}{t(a-x)}$ are 0·036 for aniline, 0·038 for *p*-toluidine, and 0·041 for *m*-xylidine, with one molecular proportion of free acid at 0°. At higher temperatures, the rate is increased (Hantzsch and Schumann, Ber. 1899, 32, 1691; 1900, 33, 527). Both colorimetric and electrolytic determinations of the velocity of diazotisation show that, in the absence of disturbing influences, all the aromatic amines are diazotised at the same rate.

ALTERNATIVE METHODS OF PRODUCING AROMATIC DIAZONIUM SALTS.

Nitrosyl chloride or *bromide* has been suggested as a diazotising agent (Tilden and Millar, Chem. Soc. Proc. 1894, 59; Kastle and Keiser, Amer. Chem. J. 1895, 17, 91). *Nitrosyl sulphate* has been used with advantage (Pabst and Girard, D. R. P. 6034; Ber. 1879, 12, 365; Morgan and Micklethwait, Chem. Soc. Trans. 1910, 97, 2558). *Barium nitrite*, when employed in conjunction with sulphuric acid, furnishes diazo- solutions free from inorganic salts (Witt, Ber. 1903, 36, 4388). The last-named investigator has brought forward an interesting process which consists in dissolving the base in cold concentrated *nitric acid* and adding the calculated amount of *potassium metabisulphite* required to produce sufficient nitrous acid for the diazotisation (Ber. 1909, 42, 2953).

Diazonium bromides are formed by the interaction of *hydrazines* and *diazonium perbromides*

$$2R{\cdot}N_2Br_3+RN_2H_3=3R{\cdot}N_2{\cdot}Br+3HBr$$

(Chattaway, Chem. Soc. Trans. 1908, 93, 958). An *electrolytic* process for the production of diazonium salts has been patented (Boehringer & Sons, D. R. P. 152926, and Eng. Pat. 2608 of 1904).

Diazonium salts can also be prepared from compounds not containing amino- groups; mercury diphenyl and nitrous fumes give benzenediazonium nitrate (Ber. 1897, 30, 509), and the same salt is produced from nitrosobenzene and nitric oxide in chloroform solution (*ibid.* 1898, 31, 1528). Fuming nitric acid reverses the coupling process and regenerates the diazonium salt from its azo- derivatives (Meldola, Chem. Soc. Trans. 1889, 55, 608; 1894, 65, 841; and O. Schmidt, Ber. 1905, 38, 3201).

Certain complex or highly substituted amines resist diazotisation unless treated under pressure (D. R. P. 143450) or with excess of nitrous and mineral acids (Annalen, 1873, 165, 187; 1891, 260, 224; Ber. 1900, 33, 520).

(For indirect methods of forming diazonium salts, *v.* Annalen, 1879, 199, 320; 1888, 243, 282; 1892, 270, 116; Ber. 1893, 26, 2190; 1899, 32, 1809; 1900, 33, 1718; J. pr. Chem. 1896, [ii.] 54, 496; Gazz. chim. ital. 1900, 30, 1526; Bull. Soc. Chim. 1891, [iii.] 6, 94.)

REACTIONS OF AROMATIC DIAZONIUM SALTS.

In addition to their power of coupling with phenols, aromatic amines, and their sulphonic acids to form the technically important azo-colouring matters, the diazonium salts are synthetical agents of the greatest value, and the following is a synopsis of the principal reactions in which they take part:—

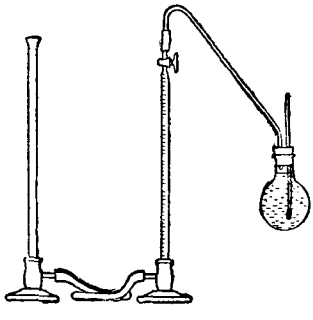
1. Decomposition of Diazonium Salts by Water.

(*Cf.* Ber. 1874, 7, 1061; 1894, 17, 2704; 1899, 32, 1773; 1890, 23, 3635; 1902, 35, 89; J. pr. Chem. 1881, [ii.] 24, 476; Chem. Soc. Trans. 1902, 81, 77; 1903, 83, 688; 1905, 87, 5; 1906, 89, 19.)

The decomposition of soluble diazonium salts by water is a unimolecular reaction, and is represented by the well-known equation:

$$C=\frac{1}{t}\log\frac{A}{A-x}$$

The relative stability of the diazonium salts is ascertained by comparing the values of the constant C for a given temperature. The most successful method of making this determination consists in heating solutions of the diazo- compounds at a fixed temperature, and measuring the rate at which nitrogen is evolved. A convenient apparatus, which can be used in this determination and also for studying the decomposition of diazo- compounds in general, is indicated in the following figure.



These quantitative decompositions show that the diazonium salts from aniline and ortho- and meta-toluidine are among the least stable of the series, whereas considerably greater stability is exhibited by the diazotised nitranilines and the diazonium sulphonates derived from the benzenoid and naphthalenoid amino-sulphonic acids.

The rate of decomposition of diazo- compounds increases with the temperature, and in

accordance with Arrhenius's formula for the temperature coefficient

$$C_{t_1}=C_{t_0}\,\frac{\epsilon A(T_1-T_0)}{T_1T_0}$$

The rate of decomposition is independent of the quantity of mineral acid present, and equivalent solutions of benzenediazonium chloride, bromide, sulphate, nitrate, and oxalate decompose with the same velocity; this change is, however, accelerated by colloidal platinum or silver, owing to catalytic action (Hantzsch, Ber. 1900, 33, 2517; Hausser and Muller, Bull. Soc. chim. 1892, [iii.] 7, 721; 1893, 9, 353; Compt. rend. 1892, 114, 549, 669, 760, 1438; Schwalbe, Zeitsch. Farb. Ind. 1905, 4, 433; Ber. 1905, 38, 2196, 3071; Cain, Chem. Soc. Trans. 1902, 81, 1412; 1903, 83, 206, 470; 1905, 38, 2511; Euler, Annalen, 1902, 325, 292).

In general, the decomposition of a diazonium salt by water leads to the formation of a phenol

$$R{\cdot}N_2{\cdot}HSO_4+H_2O=R{\cdot}OH+H_2SO_4+N_2.$$

The sulphate is the best salt to employ in this reaction, because the chloride and nitrate are apt to lead respectively to alternative or secondary changes. Benzenediazonium sulphate and its homologues furnish phenol and the cresols and xylenols; diphenyl-4:4'-bisdiazonium sulphate gives rise to 4:4'-dihydroxydiphenyl. Aurin is similarly obtained from diazotised rosaniline (Annalen, 1878, 194, 306).

In certain cases, more especially in the naphthalene series, the product is contaminated by azo- compounds, resulting from the coupling of the hydroxy- derivative with a portion of the still undecomposed diazonium salt (Chem. Soc. Trans. 1903, 83, 221). To obviate this difficulty, so far as possible, excess of acid is used in the decomposition. The manufacture of the α-naphtholsulphonic acids (*e.g.* $OH:SO_3H=1:4$ and 1:8) from the corresponding α-naphthylaminesulphonic acids and the production of 1:8-dihydroxynaphthalene-3:6-disulphonic acid (chromotrope acid), are typical examples of the technical application of the process.

Secondary reactions occur even in the simplest cases (Ber. 1890, 23, 3705), and in many instances, where the boiling is protracted owing to the great stability of the diazo- compound, not a trace of the hydroxy- derivative can be isolated (Amer. Chem. J. 1889, 11, 319; Cain, Chem. Soc. Trans. 1903, 83, 688). When the phenolic product is volatile in steam, the normal change is facilitated by operating with solutions boiling above 100°. A good yield of guaiacol is obtained by adding the diazo- salt of orthoanisidine to a mixture of sodium sulphate and dilute sulphuric acid boiling at 135°–145°, the volatile product being removed at the moment of formation (Kalle & Co., Eng. Pat. 7233 of 1897; *cf.* Annalen, 1889, 253, 281; Ber. 1874, 7, 1008; D. R. P. 167211; Chem. Soc. Trans. 1906, 87, 19).

(For other exceptional decompositions of diazo- compounds, *v.* Ber. 1874, 7, 1061; 1884, 17, 2704; 1899, 32, 1773; 1902, 35, 89; Chem. Soc. Trans. 1896, 69, 1327; 1902, 81, 77, 1905; 87, 5; 1906, 89, 19.)

The diazo- compounds are very sensitive to light, which induces the phenolic decomposition even in certain cases where the action of hot water or acids is very slight (Chem. Soc. Trans. 1907, 91, 35; *cf.* Compt. rend. 1881, 92, 1074; Ber. 1890, 23, 3131; 1901, 34, 1668; D. R. PP. 53455, 56606; J. Soc. Chem. Ind. 1890, 9, 1001).

2. Decomposition of Diazonium Salts by Alcohols.

The reaction between diazonium salts and alcohols may proceed in two different ways:

1. $R{\cdot}N_2{\cdot}X+C_2H_5{\cdot}OH=R{\cdot}H+C_2H_4O+N_2+HX.$
2. $R{\cdot}N_2{\cdot}X+C_2H_5OH=R{\cdot}O{\cdot}C_2H_5+N_2+HX,$

The former of these changes was originally regarded as the general reaction, but more recent researches have shown that the second is the normal change. The factors determining the course of the reaction are, however, numerous and complicated, involving (1) the nature of the alcohol; (2) the influence of substituents in the diazonium salt; (3) the pressure and temperature at which the decomposition is effected.

The tendency to replace the diazo- group by hydrogen increases with the molecular weight of the alcohol employed. Benzenediazonium chloride or sulphate and methyl alcohol give anisole exclusively. With ethyl alcohol, these salts yield chiefly phenetole, but benzene is also produced. The diazonium sulphates from *p*-chloro- and *p*-bromo-aniline furnish only *p*-chloro- and *p*-bromo-benzene with ethyl alcohol, but with methyl alcohol they give rise mainly to the methyl ethers of *p*-chloro- and *p*-bromo-phenol (Amer. Chem. J. 1898, 20, 229; *cf.* Annalen, 1871, 159, 191; Ber. 1901, 34, 3337; 1903, 36, 2061; Amer. Chem. J. 1893, 15, 518; 1897, 19, 531, 547, 561).

The diazo- salts of the simpler amines (aniline and its homologues) react chiefly in the direction indicated by the second of the foregoing equations, and yield mixed ethers, but the presence of acid substituents

(Cl, Br, NO_2, CO_2H, $NH{\cdot}SO_2R$)

favours the predominance of the first change. The nitranilines (ortho-, meta-, and para-) give respectively 87, 51, and 40 p.c. of nitrobenzene the 1:2-, 2:1-, and 1:4-nitronaphthylamines furnish the corresponding nitronaphthalenes, whereas α- and β- naphthylamines yield α- and β-ethoxynaphthalenes (Remsen and others, Ber. 1885, 18, 65; Amer. Chem. J. 1886, 8, 243; 1887, 9, 587; 1891, 13, 153; 1892, 14, 15).

The yield of alkyl ether increases with rise of pressure, but the addition of zinc-dust or an alkali (sodium hydroxide or ethoxide, potassium carbonate) inhibits almost entirely the formation of mixed ether and leads to the substitution of the diazo- group by hydrogen (Amer. Chem. J. 1893, 15, 105, 301, 320, 379; 1894, 16, 235; 1895, 17, 454; 1897, 19, 163, 531; 1898, 20, 298; 1904, 31, 119).

3. Replacement of the Diazo- Group by Hydrogen.

In addition to the action of alcohol, the diazo- group can be eliminated by the use of a variety of reducing agents:—

(i.) The diazonium salt is reduced to the corresponding *hydrazine* and the hydrazino- group $NH{\cdot}NH_2$ removed by boiling with *copper sulphate* (Baeyer and Pfitzinger, Ber. 1885, 18, 90, 786).

(ii.) Reduction of the diazo- compound with *alkaline sodium stannite* (Friedländer, Ber. 1889, 22, 587).

(iii.) By various other reducing agents, *stannous formate* (Ber. 1885, 18, 357; J. pr.

Chem. 1889, [ii.] 40, 97), *hypophosphorous acid* (Ber. 1902, 35, 162), *sodium hyposulphite* (*ibid.* 1907, 40, 858), *formic acid* and *copper powder* (*ibid.* 1890, 23, 1632).

4. Replacement of the Diazo- Group by Halogen, Cyanide, Cyanate, and Thiocyanate Radicles.

Fluorine may be introduced into the aromatic nucleus in place of the diazo- group by treating the diazonium salt with hydrofluoric acid. Diazoamino- compounds (*v. infra*) are also employed in bringing about this replacement, and when treated with concentrated hydrofluoric acid they yield the corresponding fluoro- derivative; fluorobenzene is thus produced from diazoaminobenzene or diazobenzenepiperidide (J. pr. Chem. 1870, [ii.] 1, 395; Ber. 1875, 8, 893; 1879, 12, 581; 1889, 22, 1846),

The first really successful process for replacing the diazo- group by *chlorine* (or *bromine*) was discovered by Sandmeyer; it consists in adding the diazotised solution to cuprous chloride (or bromide) dissolved in warm hydrochloric (or hydrobromic) acid, when nitrogen is evolved and the corresponding chloro- or bromo-derivative is produced (Ber. 1884, 17, 1633, 2650; 1885, 18, 1492, 1496; 1886, 19, 810; 1890, 23, 1628, 1880; Annalen, 1893, 273, 141).

The first stage in the *Sandmeyer reaction* is considered to be the formation of an additive compound of diazonium salt and cuprous chloride; the decomposition of this intermediate product proceeds readily only above a certain temperature, which is different for each diazonium salt (Erdmann, Annalen, 1893, 272, 141; *cf.* Votoček, Chem. Zeit. Rep. 1896, 20, 70; Hantzsch and Blagden, Ber. 1900, 33, 2544). The substitution of bromine for diazo-nitrogen follows a similar course (Phil. Trans. 1864, 154, 673; Annalen, 1866, 137, 49; Amer. Chem. J. 1891, 13, 486; Gazz. chim. ital. 1890, 20, 631).

The foregoing substitutions are also effected by the addition to solutions of diazonium chlorides or bromides of finely divided copper or the copper bronze of commerce (Gattermann, Ber. 1890, 23, 1218; 1892, 25, 1074; Ullmann, *ibid.* 1896, 29, 1878; *cf.* Angeli, *ibid.* 1891, 24, 952).

Iodine is readily substituted for the diazo-complex by treating the acid diazo- solutions with potassium iodide even in the absence of copper or cuprous salts.

The Sandmeyer reaction includes the important synthetical operation of replacing the diazo- group by a *cyanide* radicle, the diazonium salt being added to a warm solution of potassium cuprocyanide. The Gattermann process is also applicable to this synthesis, the addition of copper powder to a mixture of diazonium salt and potassium cyanide inducing a similar replacement (Ber. 1890, 23, 1218). The *cyanate* radicle is introduced in the place of the diazo- group by adding successively to a solution of diazonium salt, potassium cyanate, and copper powder (Ber. 1890, 23, 1220; 1892, 25, 1086). The *thiocyanate* group is introduced by adding potassium thiocyanate and cuprous thiocyanate to a solution of diazonium sulphate (*ibid.* 1890, 23, 738, 770).

5. Replacement of the Diazo- Group by Sulphur and Sulphur-containing Radicles.

These reactions are of importance as furnishing methods for the synthetical production of sulphonic acids.

Thiophenols or *disulphides* are obtained by treating diazonium salts with potassium xanthate and then hydrolysing the resulting aromatic xanthate (Leuckart, J. pr. Chem. 1890, [ii.] 41, 179; *cf.* Ber. 1887, 20, 349; Chem. Soc. Proc. 1895, 11, 141). Phenyl sulphide is produced by treating benzenediazonium salts with hydrogen sulphide or ammonium sulphide (Ber. 1882, 15, 1683). Benzenoid diazonium salts yield sulphides on treatment with sodium cuprous thiosulphate, but diazotised α-naphthylamine only gives α-azonaphthalene (Ber. 1901, 34, 3968).

The replacement of a diazonium by a *sulphinic* group is effected by saturating with sulphur dioxide an acid solution of diazonium sulphate and adding copper powder; nitrogen is evolved and the resulting sulphinic acid extracted with ether (Gattermann, Ber. 1899, 32, 1136).

The foregoing thiophenols, disulphides and sulphinic acids yield the corresponding *sulphonic acids* on oxidation (D. R. P. 70286; Eng. Pat. 11865 of 1892).

6. Replacement of the Diazo- Group by Nitro-, Nitroso-, and Amino- Radicles.

The introduction of a *nitro-* group is brought about either by heating the diazonium salt with nitrous acid and cuprous oxide or by mixing the diazonium sulphate with cupro-cupric sulphite and adding excess of alkali nitrite. By the latter process, 2:4:6-tribromobenzenediazonium sulphate gives 65 p.c. of 1-nitro-2:4:6-tribromobenzene and diazotised β-naphthylamine gives 25 p.c. of β-nitronaphthalene, a substance prepared with considerable difficulty by other processes (Ber. 1887, 20, 1497; 1900, 33, 2544). The introduction of a *nitroso-* group is effected by treating a diazonium chloride with alkaline potassium ferrocyanide (Ber. 1893, 26, 471). The addition of hydroxylamine to a solution of diazonium salt results in the regeneration of the original amine (Ber. 1892, 25, 372; 1902, 35, 2593, 3920).

7. Formation of Azoimides.

The introduction of the azimino- group N_3 into the aromatic nucleus is effected by the following reactions: (1) action of hydroxylamine on diazonium sulphates (Ber. 1892, 25, 372; 1893, 26, 1271; Forster and Fierz, Chem. Soc. Trans. 1907, 91, 855, 1350); (2) interaction of ammonia and diazonium perbromides; (3) direct action of sodium azide on diazonium salts in excess of sulphuric acid (Nölting and Michael, Ber. 1893, 26, 86; Forster and Fierz, Chem. Soc. Trans. 1907, 91, 1942). The last of these processes is carried out so readily that the production of an azimino- compound may be used to estimate the number of diazo- groups in a diazonium salt (Meldola and Hawkins, Chem. Soc. Proc. 1892, 8, 133; Morgan and Micklethwait, Chem. Soc. Trans. 1910, 97, 2560).

Miscellaneous substitutions, *v.* Chem. Soc. Trans. 1888, 53, 460; Amer. Chem. J. 1888, 10, 368; Ber. 1902, 35, 1964.

Condensations effected by Means of Aromatic Diazonium Salts.

Azo- compounds are formed, to a slight extent, during the Sandmeyer reaction, and this

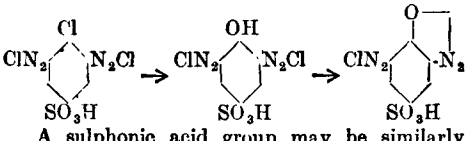
condensation takes place to a greater extent when the usual order of mixing is reversed and the cuprous chloride added to the cold solution of diazonium salt. Aniline, *o*-chloraniline, and *o*- and *p*-toluidine give considerable quantities of azo- derivatives, but the nitranilines and their homologues furnish diphenyl compounds (Niementowski, Ber. 1901, 34, 3325; Ullmann and Forgan, *ibid.* 3802; D. R. P. 126961). Cuprous oxide dissolved in ammonia or hydroxylamine also promotes the diphenyl condensation (Annalen, 1902, 320, 122), diphenyl itself being readily prepared by adding copper, zinc, or iron powder to benzenediazonium sulphate in dilute alcohol (Ber. 1890, 23, 1226); ββ-dinaphthyl is similarly produced from β-diazonaphthalene sulphate (Chem. Soc. Trans. 1895, 67, 653).

INTERCHANGE OF GROUPS IN DIAZONIUM SALTS.

The diazonium salts of the more highly substituted amines frequently undergo remarkable transformations, some of which have been suggested for use in the technical production of azo- compounds.

The dinitroanisidines, containing nitro-groups either in ortho- or para- positions with regard to the amino- group, exchange these radicles for hydroxyl during the process of diazotisation. In certain instances, the methoxyl group present in these compounds undergoes demethylation, &c., with the production of internal diazo- oxides (quinonediazides). The nitro- group is set free in the form of nitrous acid, which continues the diazotisation process on further quantities of the base (Meldola and others, Chem. Soc. Trans. 1900, 77, 1172; 1901, 79, 1076; 1902, 81, 988; 1905, 87, 1205). A sulphonic group is replaced by hydroxyl in the diazotisation of *m*-phenylenediaminedisulphonic acid (Eng. Pat. 18283 of 1903), and certain of the dinitronaphthylamines, when diazotised, yield internal diazo-oxides, owing to the initial replacement of a nitro- group by hydroxyl (Ber. 1894, 27, 2211; 1895, 28, 1951; *cf.* Chem. Soc. Trans. 1895, 67, 908).

The replacement of an acidic (electronegative) substituent by hydroxyl frequently occurs on treating the diazonium salt with alkalis.



A sulphonic acid group may be similarly eliminated as in β-naphthylamine-1:5:7-trisulphonic acid which, when diazotised and treated with weak alkali, yields naphthylene-2-diazo-1-oxide-5:7-disulphonic acid (D. R. P. 141750; Eng. Pat. 16811, 20551, of 1901; 1561, 6615, 23993, of 1902; 16995, 27372, of 1903; 4997, of 1904).

These replacements sometimes take place even when the diazo- solutions are diluted with water, or spontaneously when the diazonium base is present as the salt of a weak acid (acetate, oxalate, carbonate, &c.) (*v.* Orton, Proc. Roy. Soc. 1902, 71, 153; Chem. Soc. Trans. 1903, 83, 796; 1907, 91, 1554; Nölting and Battegay, Ber. 1906, 39, 79).

p-Chlorobenzenediazonium thiocyanate

$$Cl\cdot C_6H_4\cdot N_2\cdot CNS$$

undergoes a remarkable molecular transformation when dissolved in alcohol containing a trace of hydrochloric acid. The thiocyanate and chlorine radicles change places, and on adding ether to the solution, *p*-thiocyanobenzene diazonium chloride is precipitated (Hantzsch, Ber. 1896, 29, 947). Similarly, 2:4:6-tribromobenzenediazonium sulphate in presence of excess of potassium thiocyanate is converted into 2:4:6-trithiocyanobenzenediazonium thiocyanate and many brominated diazonium chlorides pass into chlorinated diazonium bromides (Ber. 1897, 30, 2334; 1898, 31, 1253; 1900, 33, 505; *cf.* Chem. Soc. Trans. 1902, 81, 1376). The last of these transformations has been studied quantitatively, and the following generalisations have been established:—

(i.) Bromine atoms are replaced by chlorine only when present in the ortho- or para- position with respect to the diazonium group, those in ortho- positions being most readily removed. A bromine atom in the meta- position is not affected.

(ii.) The ease of transformation increases with the number of bromine atoms present.

(iii.) The transformation constant, calculated from the equation for a unimolecular reaction $K = 1/t(\log A/A-x)$, increases with the temperature and is also influenced by the solvent, having its minimum value in water, and becoming greater as the series of alcohols is ascended.

(iv.) Diazonium salts containing two bromine atoms are stable when dry, but are rapidly transformed in ethyl alcohol; 2:4:6-tribromobenzenediazonium chloride becomes transformed in the dry state.

These changes do not occur either with iodated diazonium chlorides or with brominated diazonium fluorides (Hantzsch, Ber. 1903, 36, 2069).

CONSTITUTION OF AROMATIC DIAZONIUM SALTS.

Aromatic diazonium salts are generally soluble in water to a neutral solution, thus showing, by an absence of hydrolytic dissociation, that the diazonium base is a stronger base than the aromatic amine from which it was derived. The strength of the diazonium base has been confirmed by physico-chemical measurements.

Determinations of the electrical conductivity of solutions of benzenediazonium chloride and nitrate show that the benzenediazonium radicle is strictly comparable with other quaternary ammonium ions. The rate of migration of the benzenediazonium ion at 25° is 45·7, the corresponding constants for the methylpyridinium and tetramethylammonium ions being 44·3 and 43·6 respectively. The molecular electrical conductivity of solutions of diazonium salts increases with dilution, just as in the case of the corresponding potassium and ammonium compounds.

The affinity constant of benzenediazonium hydroxide at 0° is 70 times greater than that of ammonium hydroxides, and somewhat exceeds that of piperidine. The affinity constants of *p*-methoxybenzenediazonium and ψ-cumidinediazonium hydroxides are even greater, and approximate closely to those of the alkali hydroxides. A comparison of the electrical

conductivity experiments, with the results obtained in the hydrolysis of ethyl acetate by benzenediazonium hydroxide, shows that in $N/128$ solutions at 0°, approximately 33 p.c. of the base exists in the ionised condition (Ber. 1890, 23, 3220; 1895, 28, 1737; 1898, 31, 1612).

Benzenediazonium (*Diazobenzene*) behaves like an alkali or a complex ammonium cation.

Benzenediazonium hydroxide (*Diazobenzene hydrate* or *hydroxide*) is only known in solution, and is produced by treating aqueous benzenediazonium chloride with the calculated amount of silver oxide, or by adding barium hydroxide to a solution of benzenediazonium sulphate (Hantzsch, Ber. 1898, 31, 340). The solution is strongly alkaline, and gives at once an azo-compound with β-naphthol; the dissolved base decomposes, however, fairly rapidly even at 0°.

The striking similarity in the physical and chemical properties of the diazonium and quaternary ammonium salts suggests the existence of quinquevalent nitrogen in the former compounds, and on these grounds the following formula, formerly proposed by Blomstrand (1869), Strecker (1871), and Erlenmeyer (1874), has now been generally adopted for benzenediazonium chloride and its homologues:

$$C_6H_5—N^V(\cdots N)—Cl$$

although, for many years, the alternative configuration, $C_6H_5·N=N·Cl$, suggested by Kekulé, was usually employed.

The close analogy existing between the diazonium and alkali salts is shown further by the facility with which the former yield double salts with cobaltic nitrite and with the chlorides of platinum, gold, and mercury. Diazonium perhalides are also known, corresponding with the perhalides of potassium, rubidium, cæsium, and quaternary ammonium bases (Ber. 1895, 28, 1736, 2754).

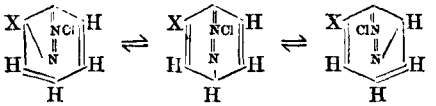
The benzenoid diazonium salts with colourless anions (nitrates, sulphates, chlorides) are generally colourless, but the corresponding bromides, iodides, and thiocyanates are coloured, and the deeper the colour the more explosive the salt. When cooled in liquid air, these coloured salts become less coloured; moreover, their aqueous solutions are colourless.

The development of colour and increase in explosibility are considered by Hantzsch to indicate a change in constitution, the coloured substance being regarded as an equilibrium mixture of diazonium salt and *syn*-diazo-compound (*v. infra*). This equilibrium is disturbed in the sense of forming more colourless diazonium salt by lowering the temperature or by dissolving the substance in water (Hantzsch, Ber. 1897, 33, 2179; 1900, 33, 2179; Euler, Ber. 1895, 31, 4168). But although in the benzene series the diazonium chlorides, nitrates, and sulphates are colourless, yet in the diphenyl and naphthalene series, many diazonium salts with these anions are coloured and comparatively stable. Moreover, this colour (yellow or orange) is retained either in aqueous solution or at the temperature of liquid air. Apart from their colour, these salts have all the properties of the simpler diazonium salts (neutral solutions, coupling with phenols, &c.). These facts indicate that increase in the complexity of the organic portion of the diazonium cation leads to the development of colour in normal diazonium salts.

(*Coloured diazonium salts*, *v.* Hantzsch, Ber. 1900, 33, 3183; 1901, 34, 4168; Annalen, 1900, 312, 126; Cain, Chem. Soc. Trans. 1905, 87, 5; Morgan and others, *ibid.* 1907, 91, 1311, 1505; 1908, 93, 614; 1909, 95, 1319.)

The idea embodied in Blomstrand's diazonium formula (*v. supra*) fails to express one important point, namely, the dependence of the stability of the diazo- complex on the presence of an unsaturated group. Yet this is a matter of fundamental importance, for hitherto no amine in which the basic nitrogen is attached to a fully saturated ring or complex has yielded a diazonium salt.

Cain has suggested an alternative formula, (2), giving expression to this circumstance (Chem. Soc. Trans. 1907, 91, 1051), in which the diazonium salt is represented as having a para-hemiquinonoid constitution; and this conception has been extended by Morgan (*ibid.* 1908, 93, 617; 1910, 97, 2563) so as to include the equally admissible ortho-hemiquinonoid configurations (1) and (3):

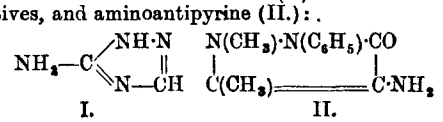


(1) (2) (3)

Euler has also advocated a para- hemiquinonoid structure for diazonium salts (Ber. 1908, 41, 3979).

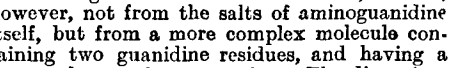
Non-aromatic Diazonium Salts.

The foregoing hypotheses of the constitution of aromatic diazonium salts, which bases their existence on the unsaturated nature of the aromatic complex, accord with the fact that certain non-aromatic primary amines containing unsaturated organic groups manifest, in some degree, the property of diazotisability. Among these bases are aminotriazole (I.) and its derivatives, and aminoantipyrine (II.):



I. II.

(Thiele and Manchot, Annalen, 1898, 303, 33; Knorr and Stolz, *ibid.* 1896, 293, 67; *cf.* Ber. 1900, 33, 1158; 1906, 39, 2925; Annalen, 1900, 312, 133). In addition to non-aromatic amines containing an unsaturated cyclic structure, it has also been shown (K. G. Hofmann, Hock and Roth, Ber. 1910, 43, 682, 1087) that aminoguanidine gives rise to diazonium salts, derived, however, not from the salts of aminoguanidine itself, but from a more complex molecule containing two guanidine residues, and having a greater degree of unsaturation. The diazonium nitrate, for example, is represented by the formula:



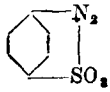
containing a diazo- complex associated with an open chain having three unsaturated linkings.

II. Cyclic Diazo- Compounds.

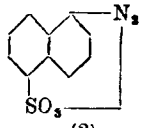
In certain instances, the action of nitrous acid on substituted aromatic amines leads to the formation of compounds having their diazo-nitrogen in a cyclic complex, this result being due to the subsequent interaction of a substituent group.

1. Internal Diazonium Salts.

Sulphonated amines of the benzene and naphthalene series furnish diazo- derivatives which are generally misnamed *diazo-sulphonic acids*. These compounds, however, do not contain ionic hydrogen, and are really internal diazonium salts; No. 1, the so-called '*diazobenzenesulphonic acid*,' being *benzenediazonium-p-sulphonate*, whilst No. 2 is *naphthalene-1-diazonium- 5-sulphonate*



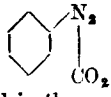
(1)



(2)

These internal diazonium sulphonates are of great technical importance in the manufacture of azo- dyes (*v.* Azo- colouring matters).

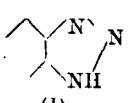
Of a similar nature are the cyclic diazo-derivatives obtained by diazotising aromatic aminocarboxylic acids (cf. Bülow and Haas, Ber, 1911, 44, 601), *e.g.* '*diazo-anthranilic acid*' or *benzenediazonium-o-carboxylate*



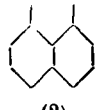
which is employed in the production of methyl red (*v.* Acidimetry and Alkalimetry).

2. Cyclic Diazo- Compounds due to Internal Condensation.

Aromatic ortho- and peri-diamines do not yield diazonium salts, inasmuch as their interaction with nitrous acid leads at once to the formation of cyclic *diazoimines* (*Aziminocompounds*)



(1)



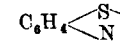
(2)

Phenylene-*o*-diazoimine (1) (*Aziminobenzene*) and **naphthylene-1:8-diazoimine** (2) (*1:8-Aziminonaphthalene*) are typical members of this series of diazo- compounds.

The triazole rings thus set up are remarkably stable, and in the case of the ortho- derivatives (No. 1) are not opened by mineral acids without complete rupture of the molecule. The peri-diazoimines (No. 2) occupy a position intermediate between the ortho-diazoimines (No. 1) and the para-diazoimines (*v. infra*).

The 1:2- and 2:3-naphthylene-diamines furnish respectively 1:2- and 2:3-*naphthylenediazoimines* (*1:2- and 2:3-aziminonaphthalenes*). (Constitution of ortho-diazoimines and their acyl- derivatives, Griess, Ber. 1882, 15, 2195; Kekulé, Lehrbuch, ii. 739; Morgan and Godden, Chem. Soc. Trans. 1910, 97, 2557; *cf.* Ber. 1874, 7, 316; 1876, 9, 221; 1887, 20, 2999; 1894, 27, 764; Annalen, 1889, 255, 344; Chem. Soc. Trans. 1906, 89, 4.)

Similar stable cyclic diazo- compounds are obtained by diazotising the ortho-aminothiophenols, **o-phenylenediazosulphide** being a colourless crystalline substance with a sweetish odour and feebly basic properties



(Jacobsen, Annalen, 1893, 277, 209, 218, 232, 237).

3. Cyclic Diazo- Compounds due to Combined Internal Condensation and Salt Formation.

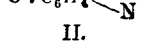
In this group are found certain diazo-derivatives of amines containing slightly acidic substituents in ortho- or para-, but not meta-positions with respect to the aminic nitrogen.

(i.) **Internal diazo- oxides** are produced from ortho- and para- aminophenols and their derivatives. In some cases, an intermediate diazonium salt is formed which condenses to the diazo-oxide on treatment with silver oxide or an alkali (Schmitt, Ber. 1868, 1, 67; Hantzsch and Davidson, *ibid.* 1896, 29, 1522; Cameron, Amer. Chem. J. 1898, 20, 229). The first diazo-compound prepared by Griess (Annalen, 1858, 106, 123), namely, **dinitrobenzenediazo-oxide**. belongs to this class; it is produced by diazotising picramic acid, and has been utilised in the production of azo- colours (D. R. P. 151332). The 1:2-, 2:1-, 2:3-, and 1:8-aminonaphthols and their sulphonic acids similarly give rise to internal diazo-oxides which are so stable that they can be nitrated. These internal diazo-oxides are readily transformed into diazonium salts by mineral acids, and are therefore available in the production of azo-dyes (Eng. Pat. 28107, of 1897; 10235, 15025, of 1904; Fr. Pat. 353786 of 1905; D. R. PP. 155083, 164665, 171024, 172446, 175593, 176618, 176619, 176620).

Internal diazo-oxides can also be produced by leaving the diazonium salts of highly substituted amines (*e.g.* 2:4:6-trichloroaniline) in aqueous solutions containing no free mineral acid (Orton, Proc. Roy. Soc. 1903, 71, 153; Chem. Soc. Trans. 1903, 83, 796).

These diazo- derivatives have been formulated either as cyclic diazo-oxides (I.) or as quinonediazides (II.):

I.

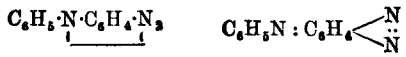


II.

(*cf.* Wolff, Annalen, 1900, 312, 126; Morgan and Micklethwait, Chem. Soc. Trans. 1908, 93, 607).

(ii.) **Para-diazoimines and diazoimides.**

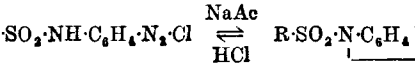
The simplest example of the para-diazoimines is obtained by the action of alkalis on the diazonium salts of *p*-aminodiphenylamine (Annalen, 1888, 243, 282; Ber. 1902, 35, 895). The following alternative formulæ (III. and IV.) have been given to this product:—



III. IV.

corresponding respectively with the foregoing formulæ (I. and II.) for the internal diazo-oxides. Successive nitration of the phenyl group gradually increases the stability of these *p*-diazoimines (Chem. Soc. Trans. 1908, 93, 604).

The para- diazoimides are produced from the acyl- and aryl-sulphonyl- derivatives of the para-diamines, and similar products are obtained from the arylsulphonyl-1 : 8-naphthylenediamines. The production of these diazoimides takes place in two stages, the diazonium salt first produced being decomposed by sodium acetate or mild alkali, yielding the internal condensation product:



V. VI.

These para-diazoimides (VI.) are yellow sparingly soluble substances readily reconverted by strong acids into the corresponding diazonium salts. They combine additively with phenols, naphthols, naphthylamines, and their sulphonic acids, yielding azo- colouring matters (Morgan and Micklethwait, J. Soc Dyers and Colourists, 1909, 25, 107; *cf.* Chem. Soc. Trans. 1905, 87, 74, 921, 1302; 1906, 89, 1162; 1907, 91, 1509; 1908, 93, 615; Badische Anilin- und Soda-Fabrik. D. R. P. 205037).

III. Diazoamines.

The diazoamines or diazoamino- compounds have the general formula $XN_2 \cdot NHY$, and may be either aromatic, mixed aromatic-aliphatic, or aliphatic in character, according as to whether X and Y are aromatic or aliphatic hydrocarbon radicles.

1. Aromatic Diazoamines.

The aromatic diazoamines are produced (1) by the action of nitrous acid (1 molecule) on two molecular proportions of a primary benzenoid amine; (2) by coupling a diazonium salt with a primary or secondary benzenoid amine.

Diazoaminobenzene $C_6H_5 \cdot N_2 \cdot NH \cdot C_6H_5$, yellow crystals, m.p. 98°, is produced in quantitative yield by dissolving 10 parts of aniline in two parts of water containing 12 parts of hydrogen chloride, diazotising with 8 parts of sodium nitrite, and adding the diazo- solution to a solution of 10 parts of aniline in the calculated amount of hydrochloric acid. The diazoamine is precipitated on the addition of sodium acetate.

When warmed with aniline containing aniline hydrochloride, diazoaminobenzene is transformed into *p*-aminoazobenzene (*v.* Azo-colouring matters), the velocity of transformation obeying the law of unimolecular reactions.

Diazoamino-*p*-toluene $C_7H_7 \cdot N_2 \cdot NH \cdot C_7H_7$, is prepared in a similar manner, and undergoes transformation into an ortho-azo- compound, but the velocity of this change is only about one-ninth of that of the preceding transformation to para-azo- derivative.

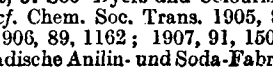
The coupling of diazonium salts with metaphenylenediamine, diphenylamine, the naphthylamines and their alkyl derivatives, leads directly to the production of azo- derivatives; in these cases, intermediate diazoamines have not been isolated, except when the reactive ortho- or para- positions are already substituted (Morgan, Chem. Soc. Trans. 1902, 81, 91; 1907, 91, 370).

When an aromatic base, XNH_2, is coupled with a diazonium salt YN_2Cl, the resulting diazoamine is identical with that produced from XN_2Cl and YNH_2, and is generally regarded as being an equilibrium mixture of the two isomerides $XNH \cdot N_2Y$ and $XN_2 \cdot NHY$. This explanation assumes the migration of the diazo-group which has been observed to occur in several instances (Ber. 1882, 15, 2190; 1896, 29, 287; 1897, 30, 1412).

(For the constitution of the unsymmetrical aromatic diazoamines, $XNH \cdot N_2Y$, *v.* Meldola and Streatfeild, Chem. Soc. Trans. 1886, 49, 624; 1887, 57, 102, 434; 1886, 53, 664; 1889, 55, 412; 1890, 57, 785; *cf.* Forster and Garland, *ibid.* 1909, 95, 2051.)

2. Aliphatic-aromatic Diazoamines.

The diazoamines containing one aliphatic and one aromatic group can be produced by (1) coupling a diazonium salt with an aliphatic amine (Ber. 1888, 21, 1016, 1112; 1889, 22, 938, 1302); (2) by treating an azide with Grignard reagent:



(Dimroth, Ber. 1903, 36, 909; 1905, 38, 670, 2328; 1907, 40, 2390). Diazoamines present the possibility of stereoisomerism, but their relative stability and the fact that they couple only slowly with β-naphthol, confirm the view that they are generally *anti*-diazo- compounds.

(For stereoisomeric diazoamines, *v.* J. Russ. Phys. Chem. Soc. 1906, 38, 587; Zeitsch. angew. Chem. 1900, 13, 762; 1902, 15, 1209.)

Aromatic bisdiazoamino- compounds, e.g. $(C_6H_5 \cdot N_2)_2N \cdot C_6H_5$, have been obtained by the action of 2 molecular proportions of a diazonium salt on one of an aromatic amine (Ber. 1894, 27, 1863, 2597; 1895, 28, 170).

Mixed aliphatic-aromatic bisdiazoamino- derivatives (*v.* Ber. 1888, 21, 1016; 1889, 22, 933; 1907, 40, 2390).

Diazo-ψ-semicarbazines (*v.* Forster, Chem. Soc. Trans. 1906, 89, 223).

3. Aliphatic Diazoamines.

Dimroth's general method may be applied to the production of purely aliphatic diazoamino- compounds. In this way, the simplest member of the series, **diazoaminomethane (dimethyltriazene)** $CH_3N:N \cdot NH \cdot CH_3$, has been prepared from methyl azide and magnesium methyl iodide. This substance, which is isolated by distilling its copper derivative with diazoaminobenzene under reduced pressure, is a colourless liquid, solidifying at −12° and boiling at 92° (Dimroth, Ber. 1905, 38, 1575; 1906, 39, 3905).

IV. Diazo- Oxides.

When a diazonium salt couples with a phenol the product is generally an ortho- or a para-hydroxyazo- compound (the C-azo- derivative),

but in all probability, the O-azo- derivative is first produced, for in a few instances, when the velocity of transformation has been lessened by substitution, the intermediate O-azo- compound or diazo-oxide has been isolated. *p*-Bromobenzenediazonium chloride and *p*-nitrophenol give *p-bromobenzenediazo-4 oxynitrobenzene*

$$C_6H_4Br{\cdot}N{:}N{\cdot}O{\cdot}C_6H_4{\cdot}NO_2,$$

which, at 80°, becomes transformed into its isomeride, *p-bromobenzene-2-azo-4-nitrophenol*

$$C_6H_4BrN{:}N{\cdot}C_6H_4(NO_2)OH$$

(Ber. 1908, 41, 4027, 4304).

Occasionally traces of these intermediate diazoamines and diazo-oxides can be detected in the commercial azo- colouring matters (Vaubel, Zeitsch. Farben. Textil. Ind. 1902, 1, 3).

V. Metallic Derivatives of Diazo-Compounds.

In 1894 Schraube and Schmidt (Ber. 27, 514) found that on adding a 10 p.c. solution of *p*-nitrobenzenediazonium chloride to 18 p.c. aqueous sodium hydroxide at 50°–60°, a sodium diazo- derivative separated in golden-yellow leaflets, to which they gave the formula

$$NO_2{\cdot}C_6H_4{\cdot}NNa{\cdot}NO,H_2O,$$

regarding the compound as the *sodium* derivative of *p-nitrophenylnitrosamine*. This view of the constitution of the product was confirmed by the action on the compound of methyl iodide when *p*-nitrophenylmethylnitrosamine

$$NO_2{\cdot}C_6H_4{\cdot}N(CH_3){\cdot}NO$$

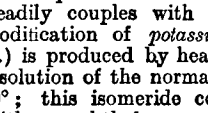
was obtained.

This sodium salt, which was regarded by Hantzsch as having the constitution of an anti-diazo- compound, **sodium *p*-nitrobenzenediazo-oxide** (*v. infra*), has been manufactured for use in the production of 'nitrosamine red' (Badische Anilin- und Soda-Fabrik D. R. PP. 78874, 80263, 81134, 81202). The addition of excess of mineral acid to this metallic diazo- derivative, determines the regeneration of the original diazonium salt, but treatment with dilute acetic acid leads to the formation of a yellow product, *p-nitrophenylnitrosamine* $NO_2{\cdot}C_6H_4{\cdot}NH{\cdot}NO$, a substance showing little tendency to couple with β-naphthol.

The silver derivative obtained from the foregoing sodium salt yields on methylation an oxygen ether $NO_2{\cdot}C_6H_4{\cdot}N{:}N{\cdot}O{\cdot}CH_3$, a reaction suggesting the possibility of tautomeric change. In many instances, two isomeric modifications of these metallic diazo- derivatives have been isolated.

Benzenediazonium chloride and cold concentrated potassium hydroxide yield the normal *labile* form of *potassium benzenediazo-oxide* (I.), which readily couples with β-naphthol. The *stable* modification of *potassium benzenediazo-oxide* (II.) is produced by heating the strongly alkaline solution of the normal or labile salt at 130°–140°; this isomeride couples only very slowly with β-naphthol.

According to Hantzsch, these isomerides have respectively the following formulæ:—



I. *Syn-* (labile form). II. *Anti-* (stable form).

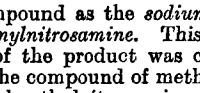
Dobbie and Tinkler (Chem. Soc. Trans. 1905, 87, 273) have found, however, that these isomeric potassium salts have totally different ultra-violet absorption spectra. But as stereoisomerides, like the benzaldoximes, have identical absorption spectra, it seems probable that the above isomeric salts are structurally dissimilar. Confirmation of the stereochemical theory would be obtained by isolating the *anti-* diazohydroxide from the stable (*anti-*) potassium salt, but on treating this with an acid, the nitrosamine separates. Moreover, the product supposed by Hantzsch and Pohl to be an *anti-* diazohydroxide (Ber. 1902, 35, 2964) was shown by Orton to be a mixture of quinonediazide and a hydroxyazo- compound (Proc. Roy. Soc. 1903, 71, 153; Chem. Soc. Trans. 1903, 83, 796).

The existence of the *syn-* diazohydroxides is doubtful, and diazonium hydroxides (*v. supra*) are only known in solution.

Diazo- anhydrides $R{\cdot}N{:}N{\cdot}O{\cdot}N{:}NR$ or $R{\cdot}\overset{\cdots}{N}{\cdot}O{\cdot}N{:}NR$ are very unstable explosive compounds produced by the action of acetic acid on the metallic *syn-* diazo-oxides. The *anti-* diazo-oxides, when thus treated, give nitrosamines.

VI. Diazo- Cyanides.

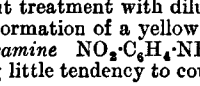
The addition of the calculated amount of potassium cyanide to a cold acid solution of a diazonium salt determines the formation of a sparingly soluble diazo- cyanide. In many instances, two modifications of the diazo-cyanides can be distinguished, and these varieties are regarded by Hantzsch as being stereoisomeric forms. *p*-Chlorobenzenediazonium chloride, from *p*-chloraniline, yields first the yellow labile *syn-p-***chlorobenzenediazocyanide** (I.), which readily evolves nitrogen, yields



I. *Syn*-diazocyanide. II. *Anti*-diazocyanide.

p-chlorobenzonitrile on treatment with copper powder, and passes into the stable *anti-p-***chlorobenzenediazocyanide** (II.). The latter substance, which is not affected by copper powder, may be distilled in steam without decomposition.

Confirmation of this stereochemical theory of the constitution of the diazo-cyanides has been obtained by a study of the cyanides derived from *p*-methoxybenzenediazonium chloride. This salt with potassium cyanide in alcoholic solution yields the *syn*-diazocyanide (III.), an orange-red insoluble substance (m.p. 51°), which couples with β-naphthol and slowly changes into the non-coupling *anti-* diazocyanide (IV.), a brownish-red compound, melting at 121°.



III. IV.

The existence of a third isomeric cyanide is indicated by evaporating at the ordinary temperature in the presence of excess of hydrocyanic acid, an aqueous solution of *p*-methoxybenzenediazonium hydroxide. The colourless crystalline product has the composition:

$$CH_3O{\cdot}C_6H_4{\cdot}N_2{\cdot}CN,HCN,2H_2O,$$

and possesses all the properties of a true metallic salt; it is very soluble, and its solution is an electrolyte. Moreover, this double salt couples with β-naphthol, and is converted by alkalis into the yellow *syn*-diazo- cyanide. These properties correspond with those of the normal diazonium salts, and the foregoing soluble cyanide is regarded as having the following constitution:

$$CH_3{\cdot}O{\cdot}C_6H_4{\cdot}\overset{\cdot\cdot}{N}{\cdot}CN$$

(Hantzsch, Ber. 1900, 33, 2161; 1904, 34, 4166).

The two pairs of diazo- cyanides from *p*-chloraniline and *p*-anisidine were examined spectroscopically by Dobbie and Tinkler, who found that each pair gave almost identical ultra-violet absorption spectra, whereas the above soluble diazonium cyanide gave an entirely different spectrum. These results are in accordance with Hantzsch's view of the configuration of the diazo- and diazonium cyanides (Chem. Soc. Trans. 1905, 87, 273).

It has, however, been suggested by several workers in this field that the isomerism of the diazo- cyanides is structural, the *syn*- compounds being *iso*-cyanides R·N:N·NC and their *anti*-isomerides, cyanides R·N:N·CN (Ber. 1895, 28, 861; Chem. Soc. Trans. 1903, 83, 805).

VII. Diazo- Sulphonates.

Although the stereochemical theory of the constitution of diazo- cyanides is supported by physical as well as chemical evidence, yet it is significant that the only other series of salts in which this isomerism has been detected is one derived from sulphurous acid, a substance resembling hydrocyanic acid in giving rise to organic isomeric derivatives which are structurally dissimilar.

The diazo- sulphonates, prepared by adding potassium sulphite to aqueous solutions of benzenoid diazonium chlorides, frequently exist in two differently coloured modifications, but in most cases the *syn*- isomeride is too unstable to be isolated in a pure state.

Potassium syn-2:4-diiodobenzenediazosulphonate (I.) is an orange substance, whilst the *anti*-salt (II.) is yellow:

$$\begin{array}{ll} C_6H_2I_2{\cdot}N & C_6H_2I_2{\cdot}N \\ \| & \| \\ KSO_3{\cdot}N & N{\cdot}SO_3K \\ \text{I.} & \text{II.} \end{array}$$

The diazotised naphthylamines behave exceptionally, yielding only *syn*-diazosulphonates, which, on warming pass, not into their *anti*-isomerides, but into the corresponding azonaphthalenes (Ber. 1897, 30, 71).

The *syn*- and *anti*- modifications of **potassium benzenediazosulphonate** $C_6H_5{\cdot}N:N{\cdot}SO_3K$, were found by Dobbie and Tinkler (*l.c.*) to have identical ultra-violet absorption spectra. This fact supports the stereochemical theory of their structures (*cf.* Ber. 1894, 27, 1726, 2099, 2586, 2930, 3527; 1895, 28, 242, 447, 834, 861; J. pr. Chem. 1894, [ii.] 50, 239; Meyer and Jacobson, Lehrbuch der Org. Chem. ii. 303).

VIII. Aliphatic Diazo- Compounds.

The amines of the aliphatic series, when treated with nitrous acid, generally lose their basic nitrogen, the amino- group becoming replaced by hydroxyl. In some cases, however, the nitrogen is retained and an aliphatic diazo-compound is produced, having the general formula $RH{\cdot}C\overset{N}{\underset{N}{\|}}$ with the azo- group attached entirely to the same carbon atom.

Although glycine is converted by nitrous acid or alkyl nitrites into glycollic acid, yet its ethyl ester gives rise to **ethyl diazoacetate** $\overset{N}{\underset{N}{\|}}CH{\cdot}CO_2{\cdot}C_2H_5$, a yellow liquid freezing at 24° and boiling at 143°-144°/72 mm. (Curtius, Ber. 1883, 16, 2230).

One kilogram of ethyl aminoacetate hydrochloride and 750 grams of sodium nitrite are added successively to 2 litres of water containing 5 grams of sodium acetate. The mixture is shaken until the temperature falls to 0°; 5 c.c. of 10 p.c. sulphuric acid and 500 c.c. of ether are added and the liquids thoroughly agitated. The ethereal layer separated and the treatment with dilute acid and ether repeated until red fumes are evolved. The ethereal extracts are washed with dilute aqueous sodium carbonate till alkaline, dried with calcium chloride, and the solvent removed on the water-bath. The yield of ethyl diazoacetate is 94·7 p.c. of the calculated quantity (Silberrad, Chem. Soc. Trans. 1902, 81, 600).

With iodine, ethyl diazoacetate yields diiodoacetic acid, and with aldehydes it condenses to form ketonic esters:

$$R{\cdot}CHO + N_2{:}CH{\cdot}CO_2{\cdot}C_2H_5 \rightarrow R{\cdot}CO{\cdot}CH_2{\cdot}CO_2{\cdot}C_2H_5.$$

One of the most remarkable reactions of this diazo- ester is its condensation with benzene and its homologues, giving rise to a series of esters containing seven-membered hydrocarbon rings (Bucherer, Ber. 1896–1903, 29, 106; 30, 632, 1949; 31, 399, 402, 2004, 2241, 2247; 32, 705; 33, 184; 36, 3509; Annalen, 1908, 358, 1).

Ethyl diazoacetate, when heated with alkalis undergoes a series of complex polymeric changes (Curtius, Ber. 1885, 18, 1283; 1906, 39, 1383, 3398, 4140; 1907, 40, 84, 815, 1176, 1194, 1470; 1908, 41, 3116, 3140, 3161; J. pr. Chem. 1888, [2] 38, 408; Hantzsch, Ber. 1900, 33, 58; *cf.* Chem. Soc. Trans. 1902, 81, 598).

Diazo- derivatives are not obtained from free α-amino-carboxylic acids, and only from those amino- esters of aliphatic acids containing the amino- group in the α- position with respect to alkylated carboxyl group. The esters of those polypeptides which contain the amino-group in the α- position to a carboxyl- group can also be transformed into diazo- derivatives.

$$NH_2{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}CO_2Et \rightarrow N_2{:}CH{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}CO_2Et.$$

The α-aminoketones (*e.g.* α-aminoacetophenone $C_6H_5{\cdot}CO{\cdot}CH_2{\cdot}NH_2$) give diazo- compounds (Ber. 1904, 37, 2080), and so also do certain uric acid compounds, *e.g.* aminomethyluracil.

Diazomethane $CH_2\overset{N}{\underset{N}{\diagdown\!\diagup}}$, the simplest aliphatic diazo- compound, is prepared by adding methyl-alcoholic potassium hydroxide to an ethereal solution of nitrosomethylurethane

$$C_2H_5{\cdot}O{\cdot}CO{\cdot}N(CH_3){\cdot}NO$$

and distilling the mixture on the water-bath, when the distillate consists of an ethereal solution of the diazo- compound, the yield being 50 p.c. of the calculated quantity. This substance is also produced by the action of hydroxylamine on dichloromethylamine

$$CH_3{\cdot}NCl_2+H_2NOH=CH_2{:}N_2+H_2O+2HCl.$$

Diazomethane is a poisonous yellow gas condensing in snow and calcium chloride to a yellow liquid boiling below 0°. It is a powerful methylating agent, converting hydroxyl groups into methoxyl, and alkylating primary and secondary bases. With iodine, diazomethane gives nitrogen and methylene iodide, and aldehydes are converted into methyl ketones (*cf.* Monatsh. 1905, 26, 1295, 1311; Ber. 1907, 40, 479; 1908, 41, 3199; 1909, 42, 2559; Chem. Soc. Trans. 1908, 93, 242).

Diazomethane combines additively with unsaturated compounds; with acetylene it gives pyrazole (Ber. 1898, 31, 2910), and with ethyl fumarate it furnishes ethyl pyrazolinecarboxylate.

Diazoethane $CH_3{\cdot}CH:N_2$ **and phenyldiazomethane** $C_6H_5{\cdot}CH{:}N_2$ have both been prepared (Ber. 1902, 35, 897). The former closely resembles diazomethane, the latter is a dark-red oil.

Diazomethane should not be confused with **azomethane** $CH_3{\cdot}N{:}N{\cdot}CH_3$, the simplest azo-compound which is produced by oxidising symmetrical dimethylhydrazine (hydrazomethane) with chromic acid (Thiele, Ber. 1909, 42, 2575). Azomethane is a colourless gas condensing to a pale-yellow liquid (b.p. 1·5°).

Diazomethanedisulphonic acid, a noteworthy example of an aliphatic diazo- compound, results from the interaction of potassium cyanide and potassium bisulphite in presence of caustic potash. The solution, acidified and treated with nitrous acid, yields successively aminomethane-*disulphonic* acid and the diazo- compound. Sulphurous acid and diazomethanedisulphonic acid yield an additive compound which, on boiling, furnishes hydrazine (*v.* Pechmann, Ber. 1895, 28, 2374; 1896, 29, 2161).

Metallic diazo- derivatives of the aliphatic series are produced by treating nitrosoalkyl urethanes with concentrated caustic potash solution or ethereal potassium ethoxide. **Potassium methyldiazo-oxide** $CH_3{\cdot}N{:}N{\cdot}OK,H_2O$ separates in white crystals, when nitrosomethylurethane is added to concentrated aqueous caustic potash at 0°. **Potassium benzyldiazo-oxide**

$$C_6H_5{\cdot}CH_2{\cdot}N{:}N{\cdot}OK,H_2O$$

is similarly prepared from nitrosobenzylurethane. These metallic derivatives are very unstable; they are decomposed by water with explosive violence, yielding respectively diazomethane and phenyldiazomethane (Hantzsch and Lehmann, Ber. 1902, 35, 897).

Bibliography.—Hantzsch, Die Diazoverbindungen, Ahren's Sammlung, 1902; Morgan, Our Present Knowledge of Aromatic Diazo-Compounds, Brit. Assoc. Report, 1902; Eibner, Zur Geschichte der Aromatischen Diazoverbindungen, 1903; Cain, The Chemistry of the Diazo- Compounds, 1908. G. T. M.

DIAZOACETATE ETHYL *v.* DIAZO- COMPOUNDS.

DIAZOAMINES, DIAZOAMINO-COMPOUNDS *v.* DIAZO- COMPOUNDS.

DIAZOAMINOMETHANE *v.* DIAZO- COMPOUNDS.

DIAZOANTHRANILIC ACID *v.* DIAZO- COMPOUNDS.

DIAZOBENZENE, *Benzenediazonium* (*v.* DIAZO- COMPOUNDS).

DIAZOBENZENE SULPHONIC ACID *v.* DIAZO- COMPOUNDS.

DIAZOIMIDES, DIAZOIMINES *v.* DIAZO- COMPOUNDS.

DIAZOMETHANE. *v.* DIAZO- COMPOUNDS.

DIAZURINE *v.* AZO- COLOURING MATTERS.

DIBASIC ACIDS. *Oxalic acid series.* A numerous and important group of acids, having the general formula $C_nH_{2n-2}O_4$. The lowest member of the series is *oxalic acid* $C_2H_2O_4$, and the highest member at present known, *dicetyl-adipic acid* $C_{38}H_{74}O_4$. As the radicle C_nH_{2n} is capable of existing in a variety of ways, it follows that these acids may exist in many isomeric forms. Unlike the fatty acids, the lowest members of the oxalic acid series are solids.

The naturally occurring acids exist partly free and partly as salts or esters. Thus oxalic acid occurs chiefly as the potassium salt in different varieties of *Oxalis* and *Rumex*; malonic acid as the calcium salt is found in the sugar beet; succinic acid in amber, certain varieties of lignite, resins, turpentine oils, and animal fluids; rocellic acid in *Rocella tinctoria* (D. C.). Other members of this series are obtained by the oxidation of naturally occurring substances. Thus suberic acid is obtained by boiling cork with nitric acid; azelaic acid by the oxidation of castor oil; adipic acid by the oxidation of suet or tallow. The higher members of the series are prepared by the oxidation of members of the fatty acid series.

General methods of preparation.

(1) By the oxidation of the diprimary glycols, primary hydroxyaldehydes, dialdehydes, primary hydroxy- acids, or aldehydeacids; *e.g.* glycol, glycollic acid, glyoxal, or glyoxylic acid → oxalic acid.

(2) By the oxidation of the fatty acids or of acids of the oleic acid series; *e.g.* erucic acid → brassylic acid.

(3) By the reduction of unsaturated dicarboxylic acids; *e.g.* fumaric acid → succinic acid.

(4) By the action of silver (powder) on monoiodo- (or bromo-) fatty acids; *e.g.* β-iodopropionic acid → adipic acid.

Exception.—The reaction is abnormal when α-bromisobutyric acid is used, di- and trialkylglutaric acids being produced.

(5) By the conversion of monohalogen substituted fatty acids or of the halogen addition products of the alkylenes C_nH_{2n} into cyan-derivatives and saponification of the latter; *e.g.* cyanacetic acid → malonic acid; ethylene dicyanide → adipic acid.

(6) By the replacement of the hydrogen atoms of the CH_2 group in the malonic esters by various alkyl- groups; *e.g.* sodium malonic ester and methyl iodide → *iso*-succinic ester.

(7) By the electrolysis of concentrated solutions of potassium alkyl salts of the dicarboxylic acids; *e.g.* potassium ethyl malonate → diethyl succinate.

(8) By the introduction of acid residues into the acetoacetic esters, and decomposition of the product with alkali; *e.g.* acetosuccinic ester → succinic acid.

(9) By the decomposition of tricarboxylic acids containing two carboxyl- groups attached to the same carbon atom; *e.g.* ethanetricarboxylic acid → succinic acid.

The acids of this series behave differently on the application of heat, depending upon the position of the carboxylic groups. Oxalic acid, the first member of the series, breaks down on heating mostly into carbon dioxide, carbon monoxide, and water, and partly into carbon dioxide and formic acid. This latter decomposition is typical of those homologues of oxalic acid in which the two carboxyl- groups are attached to the same carbon atom; they are the β-dicarboxylic acids, and of these malonic acid is the type. On application of heat, malonic acid splits into acetic acid and carbon dioxide. The next class, the γ-dicarboxylic acids, in which the two carboxyl- groups are attached to adjacent carbon atoms, when heated, lose a molecule of water and pass into anhydrides. Succinic acid is the type of these acids. Acids, such as glutaric acid, in which the carboxyl- groups are attached to two carbon atoms separated by a third, behave similarly to the γ-dicarboxylic acids, but form anhydrides less readily. When the carbon atoms to which the carboxyl- groups are attached are separated by two carbon atoms, *e.g.* adipic acid, they do not influence one another on the application of heat. For these reasons, the paraffin dicarboxylic acids are arranged in different groups, the general properties of which will be discussed under MALONIC ACID, SUCCINIC ACID, and GLUTARIC ACID, which are types of the several groups mentioned above.

(For melting-points of the dibasic acids, *v.* Massol, Bull. Soc. chim. [3] 21, 578; melting-points of their esters, *v.* Schneider, Zeitsch. physikal. Chem. 22, 228; electrical conductivity of the acids, *v.* Walden, *ibid.* 8, 448; volatility in steam, *v.* Auwers, Annalen, 292, 159.)

DI-*iso*-BUTYLACETIC ACID *v.* DECATOIC ACIDS.

2·6-DI-*iso*-BUTYLPIMELIC ACID

$$CH_2[CH_2\cdot CH(C_4H_9)\cdot CO_2H]_2$$

Prepared by heating 1.5.di-*iso*-butylpentanetetracarboxylic acid at 200°–220° (Perkin and Prentice, Chem. Soc. Trans. 1891, 842); m.p. 82°–84°.

DICENTRINE *v.* VEGETO-ALKALOIDS.

DICETYLADIPIC ACID $C_{38}H_{74}O_4$. Prepared by heating dicetylbutanetetracarboxylic acid to 205° (Lean, Chem. Soc. Trans. 1894, 1016). Two isomers are thus produced, which may be separated by crystallisation from alcohol, α-acid, m.p. 42°–43°; β-acid, m.p. 32°–34°.

DICETYLIC ACID $CH(C_{16}H_{33})_2COOH$ is obtained by heating dicetylmalonic acid; m.p. 69°–70° (Guthzeit, Annalen, 206, 365).

DICETYLMALONIC ACID

$$(C_{16}H_{33})_2C(CO_2H)_2.$$

The ethyl ester is formed by treating diethylmalonic ester with sodium methoxide and cetyl iodide: the ester is decomposed with a concentrated solution of caustic potash; m.p. 86°-87° (Guthzeit, Annalen, 206, 362).

DICHLOROCARBAMIDE *v.* HYDRAZINES.

DICYANDIAMIDE, *Cyanoguanidine*

$$NH_2(NH:)C\cdot NH\cdot C:N.$$

Obtained by the polymerisation of cyanamide in aqueous solution on long standing or on warming, especially after addition of a drop of ammonia (Beilstein and Geuther, Annalen, 108, 99; 123, 241; Haag, *ibid.* 122, 22); by treating thiourea with mercuric aniline (Montecchi, Gazz. chim. ital. 28, ii. 434). Prepared by heating ammonium sulphate and sodium cyanamide on the water-bath; cyanamide separates as a yellow oil, which, after some hours, with frequent shaking, changes into dicyandiamide (Hermann, Monatsh. 1905, 1025). Soll and Stutzer (Ber. 1908, 4534) make crude calcium nitride into a paste with water and heat to boiling. The hot liquid is filtered by suction, and dicyandiamide separates out from the filtrate. Crystallises in needles; m.p. 205° (Pohl, J. pr. Chem. 77, [2] 533). By warming with dilute acids, it is transformed into *dicyandiamidine* (*guanyl urea*) $NH_2(NH:)C\cdot NH\cdot CO\cdot NH_2$. It is used in quantitative analysis to separate nickel from cobalt. The solution containing nickel and cobalt is made alkaline, and to it is added a small quantity of sugar solution. To this is added dicyandiamidine sulphate (prepared by dissolving dicyandiamide in dilute sulphuric acid), whereby the nickel salt of dicyandiamidine is precipitated, the cobalt remaining in solution. The precipitate is filtered through a Gooch crucible, dried at 115°–160°, and weighed as anhydrous nickel dicyandiamidine $Ni(C_2H_5N_4O)_2$ (Grossmann and Schück, Analyst, 1910, 247; 1909, 455; 1907, 273, 394). Dicyandiamide is reduced by zinc and dilute hydrochloric acid at the ordinary temperatures to methylamine and guanidine, the methylamine being formed by the reduction of the prussic acid first produced (Bamberger and Seeberger, Ber. 1893, 1583); a mixture of nitric and sulphuric acids converts it into nitrodicyanodiamidine (Thiele and Uhlfelder, Annalen, 303, 107); it condenses with dialkylcyanacetic or malonic esters yielding pyrimidine derivatives; thus with diethylcyanacetic ester a condensation product is obtained which yields diethylbarbituric acid on treatment with sulphuric acid (Bayer & Co., D. R. P. 165223; Chem. Zentr. 1906, i, 514). All manures containing calcium cyanamide contain also dicyandiamide, formed by the spontaneous polymerisation of the calcium cyanamide; it is not poisonous to plants if not used in too large quantities (Perotti, Atti. R. Accad. Linci, 15, i. 48; Chem. Zentr. 1909, i. 1497; Inouye, J. Soc. Chem. Ind. 1909, 1054; Aso, *ibid.*). The Cyanide-Gesellschaft (Chem. Zentr. 1904, ii. 1079; D. R. P. 154505) treat calcium carbide or a carbide-forming mixture with nitrogen, lixiviate the mass with water, and use the product, which contains calcium cyanamide, dicyandiamide, &c., as a manure (*v. also* Frank, Zeitsch. angew. Chem. 19, 835). The constitution of dicyandiamide is regarded as $NH_2(NH:)C\cdot NH\cdot C:N$ or the tautomeride $(NH_2)_2C:N\cdot C:N$ (Bamberger, Ber. 1883, 1459; 1891, 899; Biltz, J. pr. Chem. 77, [ii.] 533; Prianichnikov, J. Soc. Chem. Ind. 1909, 724).

DIDYMIN *v.* SYNTHETIC DRUGS.

DIDYMIUM *v.* PRASEODYMIUM and NEODYMIUM.

DIETHYLACETIC ACID. *Pseudo-caproic acid* (*v.* CAPROIC ACID).

DIETHYLALLOXAN *v.* ALLOXAN.

DIETHYLSAFRANIN *v.* AZINES.

DIFFUSION. In any gaseous mixture or liquid solution, even when protected from mechanical disturbances and kept at a uniform temperature throughout, the composition ultimately becomes the same at all points, whatever the original distribution of the gaseous or dissolved substances may have been. The process by which this condition is reached is termed 'diffusion,' and it depends, not on the circulation of the unequally distributed substances as a whole, but on molecular movement. According to the kinetic theory, a mass of gas which, as a whole, is at rest, is yet the scene of great activity on the part of the constituent molecules. These are endowed with a high velocity, and alter the direction of their motion only when they collide with one another or with the walls of the containing vessel. If this point of view is adopted, then the occurrence of diffusion in a mixture of irregularly distributed gases becomes intelligible. There are, moreover, many experimental grounds for extending the kinetic theory to the liquid state, and for the view that the molecules of a liquid also are in a state of constant motion. With this conception the phenomenon of diffusion of a dissolved substance is obviously in harmony.

Diffusion of Gases.

When two vessels containing different gases at the same temperature and pressure are put into free communication, each gas penetrates the other until its partial pressure is uniform in both vessels. The experimental investigation of this phenomenon on quantitative lines is not easy, but it appears to be well established that the diffusion coefficient of each gas varies from point to point of the diffusion system (*see* Loschmidt, Sitzungsber. Akad. Wiss. Wien, 1870, 61, 367; 1870, 62, 468; von Obermayer, *ibid.* 1880, 81, 1102; 1882, 85, 147, 748; 1883, 87, 188; 1887, 96, 546; Waitz, Ann. Physik, 1882, 17, 201, 351; Lonius, *ibid.* 1909, 29, 664).

When the concentration of a gas is maintained constant at one point of a system and zero at another point, a static condition of affairs is established analogous to what is observed when one end of a metal bar is kept at a high temperature and the other end at a low temperature. If, for instance, a tall cylinder, communicating freely with the atmosphere, contains at the bottom a layer of caustic alkali, there is a regular concentration gradient from the top downwards, the carbon dioxide being completely absorbed at the surface of the alkali. Provided the concentration difference between the top and bottom of the cylinder is maintained constant, a steady condition of diffusion is attained, and the rate of flow of the carbon dioxide, as deduced from the amount absorbed by the alkali, is inversely proportional to the length of the diffusion column (*see* Brown and Escombe, Phil. Trans. B, 1900, 193, 223; *also* Winkelmann, Ann. Physik, 1884, 22, 1, 152).

Much attention has been devoted to the phenomenon of diffusion across porous diaphragms, through capillary tubes, and from narrow apertures. Graham showed (*see* Chemical and Physical Researches, p. 44) that the exchange of two gases across a porous diaphragm, the pressure on the two sides remaining the same, takes place in such a way that the volumes of the gases diffused in a given time are inversely proportional to the square roots of their densities. This observation is of very great interest in connection with the kinetic theory, from the assumptions of which it follows that the mean velocity of the molecules of a gas is inversely proportional to the square root of its density. Graham's law is not accurate except when the diaphragm is extremely thin, but it is nevertheless the basis of a method for separating two gases of different densities. Thus, for instance, when a mixture of hydrogen and oxygen in the proportion of 2:1 by volume is passed at a suitable rate through a train of clay-pipe stems, the gas collected at the further end will ignite a glowing splint. By experiments of this kind it was shown that atmospheric nitrogen is a mixture of at least two gases of different density (*see* Rayleigh and Ramsay, Phil. Trans. 1895, 186, 206). The operation of separating gases by this method is termed 'atmolysis.'

In the passage of a gas through a capillary tube—'transpiration,' as it is sometimes called—friction generally plays a considerable part, but it has been found that if the diameter of the tube is small in comparison with its length and with the mean free path of the gas molecules, then the quantity of gas passing through a given tube in unit time is inversely proportional to the square root of the density (Knudsen, Ann. Physik, 1909, 28, 75).

The time required for the escape or 'effusion' of a given volume of gas through a fine aperture in a thin plate into a vacuum is approximately proportional to the square root of the density of the gas. The thinner the plate and the smaller the aperture, the more nearly is this relationship fulfilled (*see* Graham, Chemical and Physical Researches, p. 88; Bunsen, Gasometry, p. 121; Timoféeff, Zeitsch. physikal. Chem. 1890, 6, 586; Donnan, Phil. Mag. 1900, 49, 423; Emich, Monatsh. 1903, 24, 747; Knudsen, Ann. Physik, 1909, 28, 999). An apparatus for determining the relative density of two gases, based on this principle, has been described by Bunsen (*l.c.*) (*v.* SPECIFIC GRAVITY).

The passage of a gas across a diaphragm takes place, not only when the diaphragm is porous in the ordinary sense, but also when it has the power of dissolving or absorbing the gas. Thus, at high temperatures, platinum and palladium absorb considerable quantities of hydrogen, and this gas readily diffuses through the walls of a vessel made of either metal. Winkelmann (Ann. Physik, 1901, 6, 104; 1902, 8, 388) has shown that the rate of diffusion of hydrogen through glowing platinum or palladium is not, as might be expected, proportional to the pressure of the hydrogen; at lower pressures the gas diffuses relatively more rapidly. The experimental data seem to indicate that it is the atoms, not the molecules, of hydrogen which can pass through the metal. On the ability of hydrogen and the inability of other gases to diffuse through heated palladium,

there is based the osmotic cell described by Ramsay (Phil. Mag. 1894, 38, 206).

The rate of diffusion of gases across a layer of water or aqueous solution depends mainly on the solubility and the density of the gas. According to Exner, who made experiments on the diffusion of gases across a film of soap solution, the velocity is, *cæteris paribus*, directly proportional to the absorption coefficient of the gas, and inversely proportional to the square root of its density (Exner, Sitzungsber. Akad. Wiss. Wien, 1874, 70, ii. 465; *cf.* Müller, Ann. Physik, 1891, 43, 554). Other workers, who have studied the diffusion of gases through a jelly, through a layer of water supported by a plate of hydrophane, or through a rubber membrane, find that Exner's law is only an approximate statement of the facts (*see* Wroblewsky, Pogg. Ann. 1876, 158, 545; Ann. Physik, 1879, 8, 29; Hüfner, Zeitsch. physikal. Chem. 1898, 27, 227; Hagenbach, Ann. Physik, 1898, 65, 673). Except for oxygen, the diffusion coefficients of gases are smaller in gelatine solution than in pure water.

Diffusion of Dissolved Substances.

The foundation of our knowledge of this subject was laid by the classical experiments of Thomas Graham (*see* Chemical and Physical Researches, pp. 444–600). In his experiments, 700 cub. cm. of water were placed in a cylindrical jar, and then 100 cub. cm. of the solution to be diffused were carefully conveyed to the bottom of the jar by a pipette. After a suitable time, portions of 50 cub. cm. were successively drawn off; these portions were evaporated, and the amount of substance that had diffused into each layer was thus ascertained. Graham's comparative experiments on the diffusive power of different substances in aqueous solution led him to draw a distinction, which has become of the highest importance, between the behaviour of easily crystallisable substances, and that of substances which are marked by the absence of the power to crystallise. So far as diffusibility is concerned, the distinction in question is based on the following figures, representing approximate times of equal diffusion: hydrochloric acid, 1; sodium chloride, 2·3; sucrose, 7; magnesium sulphate, 7; albumin, 49; caramel, 98. The difference in diffusive power of crystalloids and colloids is very evident from these figures.

The significance of the quantitative results obtained by Graham was emphasised by Stefan (Sitzungsber. Akad. Wiss. Wien, 1878, 78, ii. 957; 1879, 79, ii. 161), who showed that they were in harmony with Fick's diffusion law; that is, the diffusion of substances in aqueous solution is comparable with the distribution of heat in conductors. Fick's law is expressed algebraically by the formula $dS = -kq\frac{dc}{dx}dt$, where dS is the amount of substance crossing a section of the diffusion column in time dt, the sectional area of this column being q sq. cm., and dc/dx being the concentration gradient; k is known as the 'diffusion coefficient.'

The diffusion of dissolved substances, notably electrolytes, has been the subject of repeated investigation, but the method employed has not differed materially from that of Graham, described above (*see* Scheffer, Zeitsch. physikal. Chem. 1888, 2, 390; Arrhenius, *ibid.* 1892, 10, 51; Abegg, *ibid.* 1893, 11, 248; Euler, Ann. Physik, 1897, 63, 273; Abegg and Bose, Zeitsch. physikal. Chem. 1899, 1, 17; Thovert, Compt. rend. 1902, 134, 826; Graham, Proc. Roy. Soc. 1903, 72, 212; Öholm, Zeitsch. physikal. Chem. 1904, 50, 309). The general result of these investigations has been to substantiate the validity of Fick's law, although the opposite opinion also has been expressed (*see* Wiedeburg, Zeitsch. physikal. Chem. 1892, 10, 509).

Special interest has attached to the diffusion of electrolytes since the enunciation of Arrhenius's dissociation theory, according to which the ions of an electrolyte in aqueous solution are to be regarded in many respects as separate units. The researches of Kohlrausch have proved that the contribution which the one ion of an electrolyte makes to the equivalent conductivity is independent of the other ion associated with it, and Nernst has shown that the mobility which is thus characteristic of each ion must be a determining factor in the diffusive power of any electrolyte of which the ion forms a part (Zeitsch. physikal. Chem. 1888, 2, 613). He has further deduced a theoretical relationship between the diffusion coefficient of a binary electrolyte and the conductivities of the two ions, and the values of the diffusion coefficient calculated on this basis are in good agreement with the results of experimental work.

By allowing substances to diffuse into a jelly the effects of convection currents and mechanical disturbances are eliminated and the difficulties attending the experimental study of liquid diffusion are diminished. The rate of diffusion is, at most, very slightly lower in a jelly than in water at the same temperature. Experiments, in which the ends of cylinders of agar-agar jelly were immersed in aqueous solutions of various substances, have shown that the total amount of substance diffusing into the jelly is proportional to the square root of the time during which diffusion has taken place. This is a result in harmony with Fick's law (*see* Voigtländer, Zeitsch. physikal. Chem. 1889, 3, 316; *cf.* Chabry, Journ. de Physique, 1888, 7, 115; Morse and Pierce, Zeitsch. physikal. Chem. 1903, 45, 589; Hausmann, Zeitsch. anorg. Chem. 1904, 40, 110).

Experiments have been made also on the diffusion of various electrolytes and non-electrolytes in alcohol (Kawalki, Ann. Physik, 1894, 52, 166, 300; 1896, 59, 637), of various metals in mercury, fused lead, &c. (Meyer, *ibid.* 1897, 61, 225; 1898, 64, 752; Humphreys, Chem. Soc. Trans. 1896, 69, 243, 1679; Roberts-Austen, Phil. Trans. 1896, 187, 383; von Wogau, Ann. Physik, 1907, 23, 345), and of chlorine, bromine, and iodine in some organic solvents (Euler, Ann. Physik, 1897, 63, 273; Walden, Zeitsch. Elektrochem. 1906, 12, 77). In the last-mentioned connection, Walden has shown that, when a given halogen is considered, the product 'diffusion coefficient × viscosity of solvent' is a constant, independent of the nature of the solvent. The value of the product for the different halogens is inversely proportional to the square root of the molecular weight (*cf.* Pissarjewsky and Karp, Zeitsch. physikal. Chem. 1908, 63, 257).

The different rates of diffusion found by Graham for different substances suggested to him that the process of diffusion might be useful in separating the constituents of an aqueous solution. In this connection, he found that the difference in diffusive power between crystalloids and colloids, referred to above, was greatly accentuated by the interposition of a colloid membrane between solution and solvent, and the method of separation by diffusion through a septum of gelatinous matter he termed 'dialysis.' A sheet of parchment paper, for instance, is tied tightly over the end of a cylindrical or bell-shaped glass vessel, provided with a flange, and into the receptacle so formed, a 'dialyser,' as it is called, the mixed solution of crystalloids and colloids is poured. The outside of the parchment membrane is bathed with water, which is frequently renewed, and the result is that the contents of the dialyser, after a few days, are found to be practically free from crystalloids. Instead of the apparatus just described, a sausage-skin dialyser may be employed: the parchment tube is charged with the solution of crystalloid and colloid, and is hung up by its ends in a vessel of water.

Collodion may be used as a membrane instead of parchment, and it is obtainable in any desired form by the evaporation of the ordinary collodion solution (*see* Lillie, Amer. J. Physiol. 1907, 20, 127; Schryver, Proc. Physiol. Soc. 1908, 23).

Dialysis plays a considerable part in the technical production of beet sugar. In the diffusion process for the extraction of the sugar, beet cuttings are treated with hot water. Such treatment kills the protoplasm, and the cell membrane, which in the living state is impermeable to sugar, now allows this substance to pass out into the water. The high temperature also favours rapid diffusion. The albuminous substances in the beet juice, however, cannot readily penetrate even the dead protoplasm, which acts as a differential membrane, and thus leads to a dialytic separation of the sugar from some of the non-sugar constituents of the cell sap. In the treatment also of beet sugar molasses dialysis with parchment membranes is employed. The result of this procedure is to reduce the salt content of the molasses, and so make possible the crystallisation of a further portion of the sugar (*v.* SUGAR).

Diffusion of Solids.

The efficiency of certain cementation processes indicates that one solid can slowly penetrate another. The occurrence of diffusion in solids has been proved and investigated by Roberts-Austen (Phil. Trans. 1896, 187, 383), who finds that at temperatures between 100° and 200° there is an appreciable diffusion of gold into solid lead in 30 or 40 days, although the penetration is much slower than into the fluid metal. Experiments lasting over four years have shown that gold diffuses into solid lead, even at the ordinary temperature (Roberts-Austen, Proc. Roy. Soc. 1900, 67, 101).

J. C. P.

DIFORMIN *v.* FORMINS.

DIGALEN *v.* SYNTHETIC DRUGS.

DIGALLIC ACID (*Gallotannic acid, tannin*) *v.* TANNIC ACIDS.

DIGESTER *v.* AUTOCLAVE.

DIGIPURATUM *v.* SYNTHETIC DRUGS.

DIGITALINUM VERUM *v.* SYNTHETIC DRUGS.

DIGITALIS. *Foxglove.* (*Digitale*, Fr.; *Fingerhut*, Ger.) The foxglove, or *Digitalis purpurea* (Linn.), is well known throughout the British Islands and most parts of Europe for its elegant appearance and beautiful purple-crimson flowers (*cf.* Woodville, Med. Bot. 24; Bentl. a. Trim. 195). Foxglove is a powerful arterial sedative, reducing the force and frequency of the heart's action, and has been in use in medicine since the sixteenth century. The leaves are generally employed, but the seed possesses a like activity. (For time of gathering, *see* Brit. Pharm. 1885; Schneider, Bull. Pharm. 1870, 164; Nativelle, J. Pharm. Chim. [4] 20, 81.)

Numerous attempts have been made to isolate the constituent or constituents upon which the physiological action of digitalis depends, and more or less definite substances have been from time to time announced, the relation of which to one another is at the present day a matter of uncertainty. A *résumé* of the early work is given by Pereira (Mat. Med. 1850, 2, 1386). Active extractives were obtained, and variously named *digitaline, picrin,* or *scaptin,* in addition to other constituents common to plants.

Homolle was, however, the first investigator to prepare a fairly definite physiologically active substance from foxglove leaves. To obtain the *digitaline of Homolle,* a dried alcoholic extract of the leaves is exhausted with acetic acid and water, the solution purified by treatment with animal charcoal, and the soluble acetate converted into insoluble tannate, from which the digitaline is set free by the action of oxide of lead. The crude product is freed from inactive constituents by washing with ether. The digitaline thus obtained is exceedingly bitter, and irritating to the nasal membranes. It is white, inodorous, and imperfectly crystalline. It is insoluble in water and ether, but dissolves in alcohol. In sulphuric acid it dissolves brown to crimson after standing a few days, and in hydrochloric acid yellow to green. This is the digitalin which has from time to time found a place in the pharmacopœias (Homolle, J. Pharm. Chim. [3] 7, 57; Henry, *ibid.* [3] 7, 460; Homolle and Quevenne, Mémoires sur le Digitaline, Paris, 1851). It possesses the physiological activity of digitalis (Homolle; Bourchardat and Sandras, Ann. Thérap. 1845, 60).

Nativelle, in a series of communications (J. Pharm. Chim. [4] 15, 192; 9, 255; 16, 430; 20, 81), describes a *crystallised digitalin.* One method of obtaining this is to exhaust the dried leaves with alcohol, concentrate the solution, and mix with three times its bulk of water, when a precipitate comes down. The precipitate contains the digitalin, together with another compound, *digitin,* the former soluble and the latter insoluble in chloroform, and an important amorphous compound, *digitaleïn,* remains in the solution (*v.* Palm, Zeitsch. anal. Chem. 23, 22). Nativelle's digitalin consists of rosettes of slender needles, which, treated with hydrochloric acid, dissolve with an emerald-green colour. Flückiger (Neuer. Jahr. Pharm. 29, 129) employs, in the place of hydrochloric acid, warm phosphoric acid, on a watch-glass, to which a few

crystals of digitalin are added. The acid becomes yellow and the digitalin of a beautiful green colour (*cf.* Brunner, Ber. 6, 86; Zeitsch. anal. Chem. 13, 72; Lafon, Compt. rend. 100, 1463; Hock, J. 1881, 977; and Almquist, Arch. Pharm. [3] 5, 515). Digitalin is almost insoluble in water and ether, but dissolves in absolute, or, better, in 90 p.c. alcohol, and in chloroform. Digitin $C_4H_8O_2$ consists of stellate groups of needles. It is insoluble in water, very slightly soluble in ether, chloroform, and benzene, but soluble in alkalis and hot alcohol. Sulphuric acid dissolves it forming a brown to purple solution, but it gives no green colour reaction with hydrochloric acid (*cf.* Goerz, Pharm. Zeit. 1873, 385 and 417). Of the three constituents discovered by Nativelle digitaleïn is the only one, according to Goerz, possessing marked physiological activity. It is a bitter, light-yellow powder. When inhaled through the nose, it causes violent sneezing. It is soluble in water and alcohol, and nearly insoluble in ether, chloroform, and benzene. It gives the green colour reaction with hydrochloric acid, and, treated with sulphuric acid and bromine, changes to red and purple. It contains no nitrogen, and very closely resembles the digitalin of Walz, which was probably the only important active constituent in the original preparation of Homolle. Like the digitalin of Walz, digitaleïn yields, when treated with dilute acids, glucose and a compound called digitaliretin.

Schmiedeberg (Arch. exp. Path. u. Pharm. 1874, 3, 16) found that commercial digitalin contains a new constituent, digitoxin, and in addition three glucosides—digitonin, digitalin, and digitaleïn. These constituents have been investigated at great length by Kiliani (Ber. 23, 1555; 24, 239, 3951; 25, 2116; 31, 2454; Arch. Pharm. 230, 250, 261; 233, 299, 311; 234, 273, 481; 235, 425; 243, 5); Kiliani and Windaus (Arch. Pharm. 237, 466); Kiliani and Merk (Ber. 34, 3562); Kiliani and Schweissinger (*ibid.* 37, 1215). The following is a brief summary of some of the more important facts brought to light. The seeds of *Digitalis purpurea* contain (1) *digitonin*, a crystalline inactive glucoside, which forms about 50 p.c. of the glucosides present, and is useless as a therapeutic agent. On hydrolysis, it yields digitogenin, galactose, and lactose; (2) *digitoxin*, which consists of minute white crystals, insoluble in water and very active physiologically,—when hydrolysed with alcoholic hydrochloric acid, digitoxigenin and digitoxose are obtained; (3) *digitalin*, having the same physiological action as digitalis. The following are given as tests for digitalis: (*a*) a few particles treated with 2 c.c. of 10 p.c. aqueous potash should remain colourless for at least one minute, the presence of other glucosides causes immediate colouration; (*b*) the sample is stirred with water to a thin paste, 22 parts of amyl alcohol added, with shaking, for every 100 c.c. water used. If digitonin is present, this will separate out within 24 hours in small crystalline agglomerates. When digitalin is heated with strong hydrochloric acid, it yields digitaligenin $C_{16}H_{22}O_2$, dextrose and digitalose $C_7H_{14}O_5$. The existence of a definite digitaleïn is very doubtful.

Digitalis leaves contain neither digitonin nor digitalin (see, however, Keller, Chem. Zentr. 1897, i. 1211; Cloetta, *ibid.* 1901, i. 1102); but digitoxin is present and also a glucoside digitophyllin $C_{32}H_{52}O_{10}$, probably identical with the French 'digitaline crystallisée.' This is more insoluble than digitoxin, and not so easily attacked by reagents. Other compounds obtained from foxglove leaves are *digitalic* and *antirrhinic acids*, isolated by Morin (J. Pharm. Chim. [3] 7, 294); while Walz, by distilling with water, obtained *digitalosmin*, a sort of camphor, and valerianic acid (*v.* also GLUCOSIDES).

The leaves of *Digitalis purpurea* contain a yellow colouring matter, *digitoflavone* $C_{15}H_{10}O_6$ (Fleischer, Ber. 32, 1184); but this, according to Kiliani and Meyer (*ibid.* 1901, 34, 3577), is in reality *luteolin*. A. S.

DIGITALON *v.* SYNTHETIC DRUGS.

DIGITOXIN *v.* SYNTHETIC DRUGS.

DIHEPTYLACETIC ACID $(C_7H_{15})_2CH{\cdot}COOH$ is obtained by treating diheptylacetoacetic ester with potassium hydroxide (Jourdan, Annalen, 200, 116); m.p. 26°–27°.

DIHYDRAZINES *v.* HYDRAZINES.

DIHYDROXY- ACIDS *v.* HYDROXY- ACIDS.

DIHYDROXYBENZOIC ACIDS *v.* PROTOCATECHUIC ACID.

DIHYDROXYTARTARIC ACID *v.* KETONES.

DI-IODOFORM *v.* SYNTHETIC DRUGS.

DIKA-BREAD. An edible cake made by the natives of Sierra Leone and the Gaboon from the fruit of the mango tree, indigenous to most tropical climates. The fruit resembles chocolate in appearance, and contains a large quantity of fatty matter. It has occasionally ripened under hot-house cultivation in this country.

DIKA FAT GROUP. Under this name may be comprised several fats which are characterised by high saponification values, like the fats of the Cocoa Nut Oil group, but which differ from them by the absence of volatile fatty acids. The high saponification value indicates a preponderant proportion of lauric acid. These fats are further characterised by low iodine values. The most prominent of this group are: (1) **Dika fat**, obtained from the seed-kernels of various kinds of *Irvingia: I. gabonensis* (Baill.), *I. Barteri* (Hook, fil.). (2) **Tangkallak fat**, obtained from the fruits of *Lepidadenia Wightiana* (Nees; Bl.), *Cylicodaphne sebifera* (Bl.), *Tetranthera calophylla* (Miquel), *Tetranthera laurifolia* (Jacq.), *Litsea Sebifera* (Pers.), *Sebifera glutinosa* (Lour.). (3) **Irvingia butter, Cochin-China wax,** or **Cáy-cáy fat, the fat** obtained from *Irvingia Oliveri* (Pierre), *Irvingia malayana* (Oliv.), *Irvingia Harmandiana* (Pierre), *Buchanania fastigiata* (H. Baillon). The Cáy-cáy tree—'candle tree'—is a tropical tree indigenous to Cochin China and Cambodia. Large quantities of the fat are used by the natives as candles. The freshly prepared fat is employed for edible purposes. (4) **Kusu oil**, contained in the fruit of the camphor-yielding tree, *Cinnamomum camphora* (Nees), *Lauraceæ*. From its chemical characteristics, the conclusion may be drawn that it consists of pure laurin with a few per cent. only of olein. J. L.

DIKETONES *v.* KETONES.

DIKETOSUCCINIC ACID *v.* KETONES.

DILATOMETER. A term originally used to denote an apparatus for measuring the

thermal expansion of liquids. Subsequently given by Silbermann to an instrument for determining the strength of aqueous alcohol.

DILITURIC ACID, *nitrobarbituric acid, nitromalonylurea*, $CO\langle^{NH\cdot CO}_{NH\cdot CO}\rangle CH\cdot NO_2,3H_2O$, obtained by treating alloxantin first with hydrochloric acid and subsequently with nitric acid (Schlieper, Annalen, 56, 24); by warming hydurilic acid with nitric acid (Baeyer, *ibid.* 127, 211); by nitrating barbituric acid with fuming nitric acid (Baeyer, *ibid.* 130, 140); by oxidising violuric acid (nitrosobarbituric acid) (Ceresole, Ber. 16, 1134); or by oxidising with nitric acid the compound $C_{16}H_{26}O_{11}N_{12}S_2$ obtained by condensing *iso*dialuric acid with thiocarbamide (v. Vogel, Annalen, 315, 259; Bartling, *ibid.* 339, 37).

Dilituric acid crystallises in colourless quadratic prisms or plates, is sparingly soluble in cold, more readily so in hot water, is sparingly soluble in alcohol and insoluble in ether. It forms chloropicrin when warmed with bleaching powder, is reduced by hydriodic acid to *uramil* (*aminobarbituric acid*), and suffers partial reduction when heated with glycerol, yielding *violuric acid*. Dilituric acid is tribasic, but most of the salts are acidic, and contain only one equivalent of the metal; they are sparingly soluble in water, and are not generally decomposed by mineral acids. The *ammonium salt*

$$C_4H_2(NH_4)O_5N_3,$$

the *sodium salt* $C_4H_2NaO_5N_3,4H_2O$, *potassium salt* $C_4H_2KO_5N_3$, *calcium salt*

$$Ca(C_4H_2O_5N_3)_2,4H_2O,$$

the *barium compound* $BaCl(C_4H_3O_5N_3),H_2O$, *ferrous salt* $Fe(C_4H_2O_5N_3)_2,8H_2O$, and the *silver salt* $C_4H_2AgO_5N_3,2H_2O$, are colourless; the *ferric salt* $Fe(C_4H_2O_5N_3)_3,6H_2O$ is bright yellow, the *copper salt* $Cu(C_4H_2O_5N_3),H_2O$ is greenish, the *dipotassium salt* $C_4HK_2O_5N_3$ is bright-yellow (Schlieper, *l.c.*), and the *triargentic salt* $C_4Ag_3O_5N_3$ is lemon-yellow (Baeyer, Annalen, 130, 140). According to Holleman (Rec. trav. chim. 1897, 16, 162), dilituric acid and its homologues are aliphatic nitro-compounds in which the *iso*- form (*cf.* Hantzsch and Schultze, Ber. 1896, 29, 699, 2251; Hantzsch and Veit, *ibid.* 1899, 32, 607) is the stable modification. The aqueous solution of dilituric acid is faintly yellow and decomposes carbonates; the molecular conductivity for 1 gram-molecule dissolved in v litres of water is 323·4 (v=32), 341·4 (v=512), (μ_∞ should be 356); the acid is therefore almost completely dissociated in aqueous solution; the addition of one equivalent of a base does not appreciably change the colour of the solution, but on adding a second equivalent, the solution assumes the deep-yellow colour characteristic of the aqueous solutions of the salts of this acid. Assuming that the formula $CO\langle^{N=C(OH)}_{NH\cdot CO}\rangle C\cdot N\cdot OH$ (O) represents the constitution of the acid, Holleman states that the anion

$$CO\langle^{N=C(O-)}_{NH\cdot CO}\rangle C\cdot N\cdot OH \quad (O)$$

is colourless and slowly hydrolyses into the yellow anion $CO\langle^{N=C(O-)}_{NH\cdot CO}\rangle C\cdot N\cdot O-$ (O).

Methyldilituric acid, 1-*methyl*-5-*nitrobarbituric acid* $CO\langle^{NMe\cdot CO}_{NH\cdot CO}\rangle CH\cdot NO_2,1·5H_2O$, prepared by oxidising methylvioluric acid with concentrated nitric acid (Andreasch, Monatsh. 1900, 21, 281), crystallises from aqueous solution, and the anhydrous acid is colourless; it melts and decomposes at 143°, is readily soluble in hot water, less so in cold water, alcohol, or acetone, and sparingly soluble in ether. The aqueous solution of the acid is intensely yellow, and decomposes carbonates; the aqueous solutions of the salts are also yellow, but the solid salts are colourless or pale-yellow and sparingly soluble; the *potassium salt* $C_5H_4KO_5N_3$, the *sodium salt* $C_5H_4NaO_5N_3,H_2O$, the *ammonium salt* $C_5H_4(NH_4)O_5N_3$, are colourless; the *barium salt* $(C_5H_4O_5N_3)_2Ba,H_2O$, the *cadmium salt* $(C_5H_4N_3O_5)_2Cd,2H_2O$, are pale-yellow; the *strontium salt* $(C_5H_4O_5N_3)_2Sr,3H_2O$ is colourless, but becomes yellow on losing its water of crystallisation. Methyldilituric acid is stable with bases; it reacts readily with chlorine to form *methylchlordilituric acid*

$$CO\langle^{NMe\cdot CO}_{NH\cdot CO}\rangle CCl(NO_2)$$

m.p. 121°; the corresponding bromo- compound melts and decomposes at 138°–139°.

Dimethyldilituric acid, 1:3-*dimethyl*-5-*nitro-barbituric acid* $CO\langle^{NMe\cdot CO}_{NMe\cdot CO}\rangle CH\cdot NO_2$, obtained by oxidising dimethylvioluric acid with concentrated nitric acid (Techow, Ber. 27, 3085; Andreasch, Monatsh. 16, 26); forms colourless microscopic crystals from acetone; dissolves in 5·98 parts of water at 14°, is sparingly soluble in alcohol, melts at 152° and changes into dimethylalloxan (Holleman, Rec. trav. chim. 16, 162), and is reduced by hydriodic acid to dimethyluramil.

Dimethyldilituric acid is intensely yellow in aqueous solution, and this is due to the presence of the coloured anion of the *iso*nitro- form $CO\langle^{NMe\cdot CO}_{NMe\cdot CO}\rangle C:NO\cdot OH$, for on adding concentrated nitric acid, the colour almost entirely disappears; further, the molecular conductivity of the acid for 1 gram-molecule dissolved in v litres of water is 313·3 (v=32), and 337·6 (v=1024), (μ_∞ should be 352), so that in each solution the acid is almost completely ionised (Holleman, Rec. trav. chim. 16, 162). The salts of dimethyldilituric acid are coloured, the *sodium salt* $C_6H_6NaO_5N_3,H_2O$ is yellow, the *potassium salt* $C_6H_6KO_5N_3$ is greenish-yellow, the *magnesium salt* $(C_6H_6O_5N_3)_2Mg,4H_2O$ is yellowish-green, the *calcium salt* $(C_6H_6O_5N_3)_2Ca$ is bluish-green, the *strontium salt* $(C_6H_6O_5N_3)_2Sr$ is pale-green, the *barium salt*

$$(C_6H_6O_5N_3)_2Ba,2H_2O$$

is rose-red, and the *silver salt* $C_6H_6AgO_5N_3$ is greyish-violet (Andreash, *l.c.*, and Montash. 21, 295).

Dimethylchlordilituric acid

prepared by passing chlorine into an aqueous solution of dimethyldilituric acid; melts and decomposes at 150°; the corresponding *bromo-derivative* melts partially at 152° (Andreasch, *l.c.*). Dimethyldilituric acid is readily decomposed by the action of bases forming water, carbon dioxide, and dimethylnitromalonamide.

M. A. W.

DILL OIL *v.* OILS, ESSENTIAL.

DIMETHYLALLOXAN *v.* ALLOXAN.

***p* DIMETHYLAMINOBENZOPHENONE** *v.* KETONES.

DIMETHYLAMINONAPHTHAPHENAZINE *v.* AZINES.

DIMETHYLDIAMINOTOLUPHENAZINE *v.* AZINES.

DIMETHYLETHYL ACETIC ACID *v.* CAPROIC ACID.

DIMETHYLGLYOXIME (*βγ-dioximinobutane*) $CH_3{\cdot}C:N{\cdot}OH$ | , was originally obtained by $CH_3{\cdot}C:N{\cdot}OH$ Schramm, in 1883, by acting upon methyl-oximino-ethyl ketone with aqueous hydroxylamine hydrochloride (Ber. 16, 180). It is readily prepared in quantity by the following method (Gandarin, J. pr. Chem. 1908, 77, [ii.] 414):—

850 c.c. of commercial methyl ethyl ketone are mixed with 30 c.c. of hydrochloric acid of sp.gr. 1·19, and 1 litre of amyl nitrite is allowed to run in slowly with vigorous stirring. This takes 1½ hours, and the temperature should be maintained between 40°–50°. When the reaction is over, 800 grams of ice are added, followed by 378 grams of sodium hydroxide in 800 c.c. of water, and the mixture is shaken for half an hour. After standing, the layer of amyl alcohol is removed, and the aqueous liquid twice extracted with ether. 100 c.c. of the alkaline liquid are treated with the calculated amount of hydroxylamine hydrochloride, and the dimethylglyoxime produced is collected and weighed. If the original volume of the alkaline liquid is v c.c., a grams the weight of dimethylglyoxime obtained from the 100 c.c. of liquid, then the amount of hydroxylamine hydrochloride in grams required for the remaining liquid is equal to $656(v-100)a/109500$. This weight of hydroxylamine hydrochloride is dissolved in a little water, added to the alkaline liquid, and the whole warmed on the water-bath for an hour. The liquid is acidified with acetic acid, and the dimethylglyoxime, which separates, is filtered, washed, and dried. This product is sufficiently pure, but it may, if desired, be recrystallised from alcohol. Yield, 650–700 grams.

(For other methods of preparation, *v.* Biltz, Zeitsch. anal. Chem. 1909, 48, 164; Tschugaeff, Ber. 1905, 38, 2520.)

Properties.—Dimethylglyoxime forms colourless, glistening needles, and is insoluble in water, but soluble in alcohol. It melts at 234°, and begins to sublime at 215°. Its dibenzoyl derivative forms rhombic plates, melting at 223° (Diels and Stern, Ber. 1907, 40, 1629).

When boiled with soda, or heated with water at 160°, dimethylglyoxime is converted into its anhydride, *dimethylfurazan*, a colourless liquid boiling at 155° (Wolff, Ber. 1895, 28, 69). It yields a peroxide, boiling at 222°–223° (726 mm.), on oxidation with nitrogen peroxide in ethereal solution (Scholl, Ber. 1890, 23, 3490); this is reduced to the dioxime again when treated with zinc and acetic acid (Rimini, Gazz. chim. ital. 1895, 25, [ii.] 266).

Application in analysis.—Dimethylglyoxime is now an important analytical reagent, owing to its property of forming a bright scarlet insoluble nickel derivative. It thus becomes possible to estimate nickel simply and accurately, in the presence of iron, aluminium, chromium, cobalt, zinc, or manganese, all of which form soluble derivatives. In addition, an excellent qualitative test for nickel in the presence of cobalt is supplied. For the latter purpose, a pinch of the oxime is added to the solution containing excess of ammonia or sodium acetate, and the liquid boiled. A scarlet precipitate is obtained even when there is present only one part of nickel in two million parts of solution (Tschugaeff, Ber. 1905, 38, 2520; Compt. rend. 1907, 145, 679; Kraut, Zeitsch. angew. Chem. 1906, 19, 1793). 0·1 milligram of nickel can be detected in the presence of 5000 times as much cobalt.

For the quantitative estimation of nickel, the acid solution is heated nearly to boiling; a slight excess of 1 p.c. alcoholic dimethylglyoxime is added, and then a small excess of either ammonia or sodium acetate. The precipitate is filtered while hot on to a Gooch crucible, washed with hot water, and dried at 110°–120°. Its formula is $(CH_3{\cdot}C:NO)_2Ni+(CH_3{\cdot}C:NOH)_2$, and it contains 20·31 p.c. of nickel; it has no definite melting-point, but sublimes at 250°. Ammonium salts do not interfere; if the acetate method is employed, the original solution should be nearly neutralised with ammonia before adding the oxime and acetate (Brunck, Zeitsch. angew. Chem. 1907, 20, 834).

By either of the above methods, cobalt and zinc may be separated from nickel; but about twice the theoretical amount of reagent is necessary. Manganese, of course, can only be separated by the acetate method. Iron, aluminium, and chromium may be separated by the ammonia method, if tartaric acid be previously added (and, in addition, ammonium chloride in the case of chromium). Iron may also be separated in acetic acid solution, provided it is in the ferrous state (Brunck, Zeitsch. angew. Chem. 1907, 20, 1845; Prettner, Chem. Zeit. 1909, 33, 396, 411; Ivanicki, Chem. Zeit. Rep. 1908, 32, 644; Rhead, Analyst, 1910, 35, 97; *v. also* ANALYSIS).

The oxime is sufficiently expensive to make its recovery desirable. This may be effected by dissolving the nickel derivative in aqueous potassium cyanide and acidifying with acetic acid. The precipitated dimethylglyoxime is purified by recrystallisation from hot alcohol, after decolourisation with charcoal (*v.* KETONES).

DIMETHYLMALONIC ACID *v.* GLUTARIC ACID.

DIMETHYLOXALIC ACID *v.* HYDROXYBUTYRIC ACIDS.

αα-DIMETHYLPROPIONIC ACID *v.* VALERIC ACID.

DIMETHYLPYRROLE *v.* BONE OIL.

DIMETHYLSAFRANINES *v.* AZINES.

DIMETHYLTRIAZINE, *Diazoamintomethane* (*v.* DIAZO- COMPOUNDS).

DINAPHTHAZINES *v.* AZINES.

DINITROBENZENEDIAZO-OXIDE *v.* DIAZO-COMPOUNDS.

DIOCTYLMALONIC ACID

$(C_8H_{17})_2C(CO_2H)_2$.

Prepared from diethylmalonic ester, sodium methoxide and octyl iodide, and subsequent decomposition of the ester thus formed with caustic potash (Conrad and Bischoff, Annalen, 204, 163); m.p. 75°.

DIOFORM. Trade name for *symm.* 1-2-*di-chlorethylene* (acetylene dichloride) $\begin{matrix}CHCl\\ \|\\ CHCl\end{matrix}$ (*q.v.*) Suggested as an anæsthetic.

DIONIN *v.* SYNTHETIC DRUGS.

DIOSPHENOL, *Buchu camphor* (*v.* BUCHU).

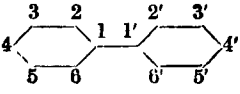
DIOXOREA. A genus of plants of the Dioxoreaceous order, the tubers of which are known as yams, and are largely eaten in the West Indies and other tropical countries. *D. batatas* (Decne) is the plant producing tubers known as 'sweet-potatos,' which are cooked and eaten as a substitute for potatos.

DIPHENAL, *Diaminohydroxydiphenol*, used as a photographic developer.

DIPHENAZINE *v.* AZINES.

***o*-DIPHENETIDINE** *v.* DIPHENYL.

DIPHENYL. This hydrocarbon, which has the molecular formula, $C_{12}H_{10}$, is structurally composed of two benzene nuclei joined together by a bond linking two carbon atoms, one in each ring. The carbon atoms are numbered for the purposes of nomenclature in the following way:—



Although of minor importance, diphenyl is nevertheless the parent substance of a large number of important bases which have found application in the preparation of the so-called substantive cotton dyes, that is to say, of colouring matters which will affix themselves to the vegetable fibres without the aid of a mordant. These bases are, however, not derived directly from the hydrocarbon, but are prepared by an indirect method which will be described later.

Diphenyl was originally obtained by Fittig (Annalen, 121, 363) from an ethereal solution of bromobenzene by the action of metallic sodium

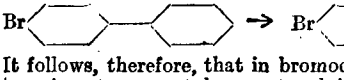
$C_6H_5Br + BrC_6H_5 + 2Na \rightarrow C_6H_5—C_6H_5 + 2NaBr$

but it is more conveniently prepared by the method discovered by Berthelot (Ann. Chim. Phys. [4] 9, 453; [4] 12, 185), who obtained it by passing the vapour of benzene through a red-hot tube

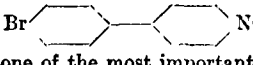
$C_6H_5H + HC_6H_5 \rightarrow C_6H_5—C_6H_5 + H_2$.

The following procedure is recommended (Schultz, Ber. 9, 547; Hubner, Annalen, 209, 339); Apparatus, La Coste and Sorger (*ibid.* 230, 5). The vapour from a quantity of benzene (free from thiophene), contained in a large flask heated on the water-bath, is allowed to pass through an iron tube, filled with pumice, which is heated to a red heat in a combustion furnace; the lower end of the iron tube is attached to a condenser and receiver, in which the products are collected. When all the benzene has distilled over, the distillate is again placed in the flask, and the vapour passed anew through the red-hot tube. The ultimate product is then fractionally distilled, and the portion boiling between 250°–260°, which solidifies on cooling, is purified by recrystallisation from alcohol. Diphenyl separates from alcohol as large, lustrous laminæ which melt at 70·5°. It boils at 254° (corr.), and is insoluble in water. The hydrocarbon, when oxidised by chromic acid, passes into benzoic acid.

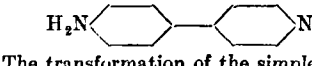
Derivatives of diphenyl and their orientation.—The more important derivatives of diphenyl are not prepared directly from the hydrocarbon, but from certain nitro- derivatives of benzene in a manner to be described later. The hydrocarbon yields, however, halogen, nitro- and sulphonic acid derivatives analogous to those prepared from benzene, substitution taking place in either one or both rings according to the conditions of the experiment. The method of orientation adopted for these compounds may be briefly described as follows (Schultz, Annalen, 174, 201; Schmidt and Schultz, *ibid.* 207, 320). When diphenyl is treated with bromine, it yields a monobromodiphenyl, a substance which, on oxidation, is converted into *p*-bromobenzoic acid, thus:



It follows, therefore, that in bromodiphenyl the bromine atom must have entered in the *para*-position with respect to the linking carbon atom. When bromodiphenyl is treated with nitric acid, it is converted into a monobromomononitrodiphenyl, a substance which, on oxidation, yields a mixture of *p*-bromobenzoic acid and *p*-nitrobenzoic acid. It is therefore apparent that the formula of this bromonitro-derivative must be:



Now, one of the most important derivatives of diphenyl is benzidine, a diamino- derivative of diphenyl, the preparation of which is described later. Since benzidine can be readily converted through its tetrazonium salt into the above bromonitrodiphenyl, it follows that benzidine must be 4-4'-diaminodiphenyl of the formula



The transformation of the simplest aromatic hydrocarbon benzene into diphenyl by the action of heat has already been mentioned. This transformation can, however, be effected much more readily by the oxidation of certain derivatives of benzene, and especially those which, like the phenols, have a reactive hydrogen in the *para*- position with respect to the substituting group. Thus phenol itself and also resorein readily pass into derivatives of diphenyl when fused with potash (Barth, Annalen, 156, 95). With hydroquinone, the transformation is still more readily effected and the action of the

mildest oxidising agents is sufficient for the purpose (Nietzki and Bernhard, Ber. 31, 1334).

The primary bases of the benzene series, such as aniline, do not lend themselves to the production of derivatives of diphenyl, but the tertiary bases readily do so; thus dimethylaniline yields tetramethylbenzidine when oxidised (Michler and Pattinson, Ber. 14, 2162 and 2164).

It has also been found that certain azo-derivatives of benzene can be transformed by oxidation into tetrazo- derivatives of diphenyl, and in this way Congo red can be formed by treating benzeneazonaphthionate with manganese dioxide and sulphuric acid:

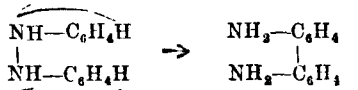
$$C_6H_5N{=}N{-}C_{10}H_5(NH_2)SO_3H$$
$$+O$$
$$C_6H_5N{=}N{-}C_{10}H_5(NH_2)SO_3H$$
$$C_6H_4{-}N{=}N{-}C_{10}H_5(NH_2)SO_3H$$
$$\rightarrow \quad | \qquad +H_2O.$$
$$C_6H_4{-}N{=}N{-}C_{10}H_5(NH_2)SO_3H$$

Derivatives of diphenyl can also be prepared from certain diazonium salts of the benzene series. Thus Kühling has shown (Ber. 28, 41; 29, 165) that when an *iso*diazo- salt is treated with an aromatic hydrocarbon in the presence of an acid chloride, the following reaction ensues:—

$$NO_2{\cdot}C_6H_4N_2OK + C_6H_6 + CH_3COCl$$
$$\rightarrow NO_2C_6H_4{-}C_6H_5 + N_2 + KCl + CH_3CO_2H.$$

This reaction has been simplified by Bamberger (Ber. 28, 403; 29, 272 and 465), who uses free *iso*diazobenzenehydrate, and shows that it passes, in the presence of benzene, without any condensing agent, into a derivative of diphenyl. Many derivatives of diphenyl can also be formed by the method of Ullmann, in which halogen derivatives of benzene are treated with finely divided copper (Ber. 43, 2682).

Benzidine and the 'Benzidine rearrangement.'—The benzidine rearrangement, which has been widely applied to the preparation of a large number of important bases used in the production of the substantive cotton dyes, is the name given to the change which an aromatic hydrazo- compound undergoes when treated with acids or certain acid reagents. The change is effected by the wandering of the hydrogen atom which is in the para- position in each ring on to the nitrogen atom attached to that ring; at the same time, the link between the nitrogen atoms is broken, and the two aromatic nuclei are joined together. It is apparent, therefore, that only those hydrazo- derivatives of benzene which have their para- positions free will undergo this transformation.



Hydrazobenzene. Benzidine.

The history of the discovery of this rearrangement is briefly as follows: Zinin (J. pr. Chem. 36, 93), in the first instance, showed that azobenzene $C_6H_5{-}N{=}N{-}C_6H_5$, when treated with alcoholic ammonium sulphide, passed into a crystalline compound which, when dissolved in alcohol and boiled with sulphuric acid, gave the sparingly soluble sulphate of a base. This base he called benzidine.

It soon became apparent that the substance responsible for the formation of benzidine must be an intermediate product formed by the action of the reducing agent on azobenzene. This view was confirmed experimentally by A. W. Hofmann (Jahresbericht, 1863, 424), who prepared the intermediate product, hydrazobenzene, and found that it passed with remarkable ease into benzidine when treated with mineral acid. Finally, Fittig (Annalen, 124, 280) showed that benzidine was identical with the base formed by the reduction of 4-4'-dinitrodiphenyl, and hence established the constitution of the base as 4-4'-diaminodiphenyl.

Preparation of benzidine in the laboratory.—Hydrazobenzene is covered with sufficient concentrated hydrochloric acid and allowed to stand for 5 minutes. Water is then added, the solution made alkaline by caustic soda, and the benzidine extracted by ether. The residue left on evaporating the ether may then either be recrystallised from water or the solution of the hydrochloride may be mixed with dilute sulphuric acid, when benzidine sulphate separates.

Technical preparation of benzidine from nitrobenzene.—10·5 parts of caustic soda are dissolved in 30 parts of water, and the solution mixed with 10 parts of nitrobenzene to which 5 parts of methylated spirit have been added. 17 parts of finely sieved zinc-dust are then added in small portions at a time, the mixture being well stirred throughout the addition. The addition of the zinc-dust sets up a vigorous reaction, and the solution boils; it is advisable to so arrange that the reacting mixture is kept at the boiling-point throughout the addition of the dust.

The contents of the vessel are now cooled, diluted with water, and carefully acidified by hydrochloric acid, the temperature being kept below 15°. The hydrazobenzene, which separates at this stage, is isolated by filtration, and converted into benzidine by boiling with dilute hydrochloric acid. The clear filtered solution of benzidine hydrochloride is then mixed with dilute sulphuric acid and the precipitated sulphate filtered and washed.

Finally, the base is prepared from the sulphate by boiling it with caustic soda solution, and is purified by distillation under diminished pressure.

Benzidine, when pure, forms colourless lustrous laminæ, which melt at 122° (127·5°–128°); it boils at 400°–401° (740 mm.). The base is characterised as a para- derivative by the formation of quinone when it is oxidised by manganese dioxide and sulphuric acid. It can be identified by a number of colour reactions: chlorine, bromine, potassium permanganate, potassium ferricyanide, and chromic acid, producing characteristic shades. The most characteristic salts of benzidine are the sulphate $C_{12}H_{12}N_2,H_2SO_4$, and the chromate $C_{12}H_{12}N_2,H_2CrO_4$. Both salts are sparingly soluble in alcohol and in water.

When treated with nitrous acid, benzidine hydrochloride is transformed into a tetrazonium salt of diphenyl

$$C_6H_4N_2Cl$$
$$|$$
$$C_6H_4N_2Cl$$

which reacts readily with the usual second components of the azo- colouring matters, forming

azo- compounds, the solutions of which possess the property of colouring the vegetable fibres without the aid of a mordant. The number of colouring matters of this kind prepared from benzidine is largely increased owing to the insoluble character of the diazonium salt

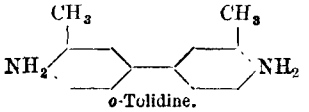
$$\begin{matrix} C_6H_4N_2X \\ | \\ C_6H_4N_2Cl \end{matrix}$$

in which one molecule of a second component, XH, has combined with the tetrazonium salt derived from benzidine. These diazonium salts can be usually isolated, and when combined with some other second component, YH, yield mixed azo- colouring matters of the formula

$$\begin{matrix} C_6H_4N_2X \\ | \\ C_6H_4N_2Y \end{matrix}$$

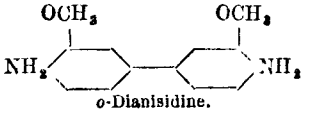
Benzidine in the presence of hydrogen peroxide is used as a test for blood, with which it gives a blue colouration. The test solution is made by taking 10 drops of a concentrated solution of benzidine in glacial acetic acid, and adding 2 c.c. of a 3 per cent. solution of H_2O_2. Sensitiveness—1 part in 200,000. (Utz, Chem. Zeit. 1907, 31, 737.)

Homologues and derivatives of benzidine used in the preparation of the substantive cotton dyes.—Although a great many of the derivatives of benzidine yield azo- colouring matters which are substantive to the vegetable fibres, yet this property is largely dependent on the position of the groups substituting the hydrogen atoms of the diphenyl molecule. Thus it has been found that when the substituting groups are in the meta- position to the coupling bond, as in



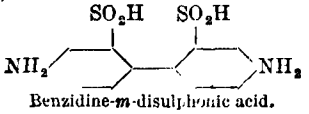
o-Tolidine.

and



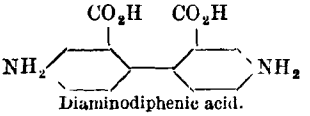
o-Dianisidine.

the azo- colours formed are substantive to cotton. If, however, groups are in the ortho-position, as in



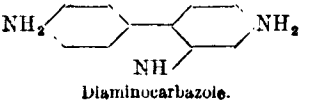
Benzidine-*m*-disulphonic acid.

and

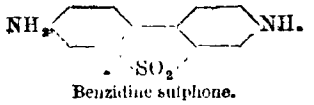


Diaminodiphenic acid.

the property of the azo- colours of dyeing unmordanted vegetable fibre is lost. The ortho-derivatives nevertheless yield substantive cotton dyes if ring formation takes place between the substituting groups in those positions; thus:



Diaminocarbazole.



Benzidine sulphone.

yield azo- dyes substantive to cotton.

The following compounds, prepared from the corresponding nitro- derivatives of benzene, are of importance:—

o-Tolidine, 4-4'-diamino-3-3'-dimethyldiphenyl $NH_2{\cdot}C_6H_3(CH_3)-C_6H_3(CH_3)NH_2$ from o-nitrotoluene, forms glistening plates, melting at 129°. It is sparingly soluble in water, but readily soluble in alcohol and in ether. The sulphate is sparingly soluble in water.

o-Dianisidine, 4-4'-diamino-3-3'-dimethoxydiphenyl $NH_2{\cdot}C_6H_3(OCH_3)-C_6H_3(OCH_3)NH_2$, from *o*-nitroanisole, forms colourless leaflets, melting at 131·5°.

o-Diphenetidine, 4-4'-diamino-3-3'-diethoxydiphenyl $NH_2{\cdot}C_6H_3(OC_2H_5)-C_6H_3(OC_2H_5)NH_2$, from *o*-nitrophenetole, forms needles or leaflets melting at 117°. J. F. T.

DIPHENYLAMINE was first obtained by Hofmann, in 1864, by distilling aniline blue (Annalen, 132, 163), and in small quantity by distilling rosaniline and leucaniline. De Laire, Girard, and Chapoteaut discovered an easier method of preparing it by heating aniline with the hydrochloride at 210°-240° (Zeitsch. Chem. 1866, 438; Compt. rend. 63, 91)

$$C_6H_5NH_2+C_6H_5NH_2HCl=NH(C_6H_5)_2+NH_4Cl.$$

It may also be obtained by heating phenol with the double compound of aniline and zinc chloride at 250°-260° (Merz and Weith, Ber. 13, 1298, 1880):

$$C_6H_5NH_2+C_6H_5OH=(C_6H_5)_2NH+H_2O,$$

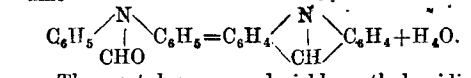
and by heating aniline and diazoaminobenzene to 150° till the evolution of nitrogen ceases. In this last reaction, ortho- and para- aminodiphenyl are formed at the same time (Hirsch, D. R. P. 62309). Diphenylamine has also been prepared by the action of aniline on bromobenzene in presence of cuprous iodide (Goldberg, D. R. P. 187870, 1906).

Manufacture.—Aniline (1 mol.) is heated with aniline hydrochloride (1 mol.) for 30-35 hours in an autoclave at 220°-230°. The product is extracted with hot dilute hydrochloric acid which dissolves the aniline hydrochloride and converts the diphenylamine into the free base, forming an oil which solidifies on cooling. The cake of diphenylamine is washed and then distilled alone or in a current of steam. Yield, 60-70 p.c. of the aniline employed. It is used in the manufacture of diphenylamine blue, diphenylamine orange, and aurantia (*v. infra*).

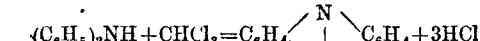
Properties.—Monoclinic laminæ; m.p. 54°; b.p. 310°; almost insoluble in water, soluble in alcohol, benzene and ether. It is feebly basic, and the salts are hydrolysed by an excess of water.

Reactions.—The hydrogen of the imino- group is replaceable by alkyl or acyl radicles. With methyl iodide it gives a methyl derivative; with benzyl chloride, a benzyl derivative. With formic or oxalic acid it yields formyldiphenylamine, m.p. 74°; with acetic acid or the acid chloride, an acetyl derivative, m.p. 103°; and with benzoyl chloride, a benzoyl derivative, m.p. 180°. When heated with zinc chloride, the

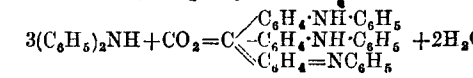
acyl derivatives lose water and form acridine derivatives. Formyldiphenylamine gives acridine



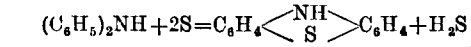
The acetyl compound yields methylacridine (Bernthsen and Bender, Ber. 1883, 16, 767). Diphenylamine also gives acridine by heating with chloroform and zinc chloride or aluminium chloride



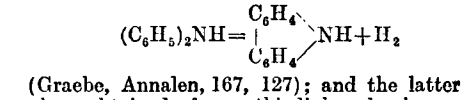
(O. Fischer and Körner, Ber. 1886, 17, 101). With excess of oxalic acid, diphenylamine is converted into diphenylamine blue



Carbon tetrachloride reacts like oxalic acid, and gives the same blue colour. With sulphur, thiodiphenylamine, the parent substance of methylene blue, is produced:



(Bernthsen, Ber. 1883, 16, 2897). When the vapour of diphenylamine is passed through a red-hot tube, carbazole is formed:



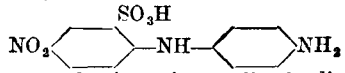
(Graebe, Annalen, 167, 127); and the latter is also obtained from thiodiphenylamine and copper powder (Goske, Ber. 1887, 20, 233).

Tests.—A solution of diphenylamine in conc. sulphuric acid gives a deep indigo-blue colour with nitric, nitrous or chloric acid. The commercial product is a pale-yellow solid, melting not much below 54°; it should contain no oil, possess no unpleasant odour, nor turn brown on exposure to air.

Derivatives.—By passing chlorine into a solution of diphenylamine in acetic acid, a tetrachlorodiphenylamine is formed. Bromine in alcoholic solution produces a tetrabromodiphenylamine; in acetic acid, a hexabromo-derivative; and at a high temperature in presence of iodine, an octo- and deca-bromo- compound. Diiododiphenylamine is formed by the action of iodine in alcoholic solution in presence of mercuric oxide. By nitration in acetic acid solution, a tetranitro- derivative is formed, whilst direct nitration yields a hexanitro- compound, crystallising in yellow prisms, and melting at 238°. The latter has strongly acid characters, and gives an ammonium salt which is used as a yellow dye known as *aurantia* (*q.v.*). Nitrosodiphenylamine is obtained by acting upon the base with amyl nitrite.

Alkyl derivatives.—Methyldiphenylamine is obtained by heating together diphenylamine (100 parts) conc. hydrochloric acid (68 parts), and methyl-alcohol (24 parts) for 10 hours to 250° in an autoclave (Girard, Bull. Soc. chim. [ii.] 23, 2). It is a liquid; b.p. 282°. The ethyl derivative is obtained in a similar way; b.p. 293°. The amyl derivative boils at 330°–340°. Benzyl chloride produces a benzyl derivative which is used in the preparation of viridine and alkali green.

Amino- derivatives.—2-Chloro-5-nitrobenzenesulphonic acid combines with *p*-phenylenediamine to form 4-nitro-4-aminoniphenylamine sulphonic acid



which, on reduction, gives *p*-diaminodiphenylamine sulphonic acid (Baeyer & Co. D. R. P. 86250, 1894). Similar derivatives are obtained by the action of *p*-aminophenol, aminophenolsulphonic acid, and *p*-aminosalicylic acid. The sulphonic acid group may be removed by heating with dilute acids under pressure (Meister, Lucius, and Brüning, D. R. P. 112180, 1899). Paraphenylenediamine and phenol in presence of copper salts and a solution of hypochlorite are oxidised to *p*-amino-*p*-hydroxydiphenylamine (Aktien Gesell. D. R. P. 204596, 1907). Diphenylamine derivatives prepared by the action of primary aromatic bases such as *p*-phenylenediamine, *p*-aminophenol, and aminosalicylic acid on (1.3.4)-dinitrochlorobenzene, (1.3.4.6)-dinitrodichlorobenzene, and (1.4.3)-nitrochlorobenzene sulphonic acid, are used in the preparation of sulphide colours, of which the most important is dinitroxydiphenylamine

$$C_6H_3(NO_2)_2NH{\cdot}C_6H_4(OH)$$

obtained from *p*-aminophenol and dinitrochlorobenzene.

Diphenylaminedicarboxylic acid is obtained by the action of anthranilic acid on *o*-chlorobenzoic acid in presence of finely divided copper. Other amino-acids behave similarly (Meister, Lucius, and Brüning, D. R. P. 148179, 1902).

Diphenylamine combines with formaldehyde, and the product forms an additive compound with sodium bisulphite

$$[(C_6H_5)_2N]_2CH_2+HSO_3Na = (C_6H_5)_2N{\cdot}CH_2{\cdot}SO_3Na+(C_6H_5)_2NH$$

(Bad. Aniline Sod. Fab. D. R. P. 158718, 1904).

J. B. C.

DIPHENYLAMINE BLUE *v.* TRIPHENYLMETHANE COLOURING MATTERS.

DIPHENYLAMINE ORANGE *v.* AZO-COLOURING MATTERS.

DIPHENYLBISDIAZONIUM CHLORIDE *v.* DIAZO- COMPOUNDS.

DIPHENYL BROWN, -CATECHINE, -CHRYSOLENES, -CITRONINE, -FAST BLACK, -FAST YELLOW, -GREEN, -ORANGE, -RED *v.* AZO-COLOURING MATTERS.

DIPHENYLENEMETHANE *v.* FLUORENE.

DIPHENYLHYDRAZINE *v.* HYDRAZINES.

DIPHENYLHYDRAZONES *v.* HYDRAZONES.

DIPHENYLMETHANE was first obtained by Jena, in 1870 (Annalen, 155, 86), by the dry distillation of barium diphenylacetate

$$[(C_6H_5)_2CH{\cdot}COO]_2Ba.$$

According to Zincke (Annalen, 159, 374), it is produced by the action of finely divided copper, iron, or zinc or their chlorides, on a mixture of benzyl chloride and benzene or by heating benzoylbenzoic acid with soda-lime. Friedel and Crafts (Bull. Soc. chim. [ii.] 41, 324) and Schwartz (Ber. 1881, 14, 1526) obtained it by the action of benzene on methylene chloride in presence of aluminium chloride; E. & O. Fischer

(Annalen, 194, 253), as a by-product in the formation of triphenylmethane from chloroform and benzene in presence of aluminium chloride; and Hirst and Cohen (Chem. Soc. Trans. 1895, 67, 826), by the action of the aluminium-mercury couple on a mixture of benzyl chloride and benzene. It is also formed by the reduction of benzophenone (Zincke, Thörner, Ber. 1877, 10, 1473; Staedel, Annalen, 194, 307; Graebe, Ber. 1874, 7, 1624). But the methods which have found a technical application in the production of diphenylmethane derivatives, as well as of the parent hydrocarbon, are those of (1) Meyer and Würster, which consists in heating a mixture of benzyl alcohol, benzene and conc. sulphuric acid (Ber. 1873, 6, 963), and of (2) Baeyer, in which benzene, formaldehyde, or methylal are shaken together in presence of conc. sulphuric acid (Ber. 1873, 6, 221).

$$CH_2O+2C_6H_6=CH_2(C_6H_5)_2+H_2O.$$

Properties.—Diphenylmethane crystallises in long, colourless, prismatic needles, possesses a fragrant smell, melts at 26°–27°, and distils without decomposition at 261°–262°. It dissolves easily in alcohol, ether, and chloroform.

Reactions.—On oxidation with chromic acid, it yields benzophenone. On passing the vapour through a red-hot tube, it is converted into *o*-diphenylenemethane. On heating it with sulphur to 250°, it gives tetraphenylethylene, and on prolonged chlorination with iodine chloride at 350° it breaks up into hexachlorobenzene and carbon tetrachloride (Ruoff, Ber. 1876, 9, 1485).

Nitro- derivatives.—On nitration, diphenylmethane yields two dinitro- derivatives, one of which melts at 183°, and the second, which is the chief product, at 118°. Other dinitro- derivatives are obtained from nitrobenzyl chloride, benzene and aluminium chloride, nitrobenzyl alcohol, benzene and sulphuric acid or nitrobenzene, formaldehyde and sulphuric acid, in a similar manner to the parent hydrocarbon. Also nitrohydroxy- derivatives can be prepared by condensing nitrophenols and their ethers with formaldehyde and conc. sulphuric acid (D. R. P. 72490). The prolonged action of nitric and sulphuric acids gives rise to a tetranitro- derivative.

Amino- derivatives.—The only substances possessing at the present time an industrial value are the amino- derivatives of diphenylmethane. They may be obtained by the reduction of the nitro- derivatives by tin and hydrochloric acid; but the more common method is to effect condensation between the aromatic base and formaldehyde, a general process for which a number of patents have been granted in recent years. Thus, by heating aniline, aniline hydrochloride and formaldehyde, 40 p.c., to 100°, 4.4′-diaminodiphenylmethane is produced (D. R. PP. 53937 and 55565). The reaction appears to occur in two stages, for on heating aniline, formaldehyde, and a strong alcoholic solution of potassium hydroxide, the following change takes place:—

$$CH_2O+2C_6H_5NH_2=C_6H_5NH\cdot CH_2\cdot NH\cdot C_6H_5+H_2O,$$

and the latter when heated with aniline and its hydrochloride passes into the diphenylmethane derivative. A tetramethyldiamino- compound is obtained in a similar manner from dimethylaniline and formaldehyde in acid solution. Similarly, a diphenyldiamino- derivative

$$C_6H_5NH\cdot C_6H_4\cdot CH_2\cdot C_6H_4NH\cdot C_6H_5$$

has been prepared from diphenylamine and formaldehyde (D. R. P. 58072), a tetramethyldiaminodihydroxy- derivative

$$(CH_3)_2N(OH)C_6H_2\cdot CH_2\cdot C_6H_3(OH)N(CH_3)_2$$

from dimethyl-*m*-amino phenol (D. R. P. 63081 and 67001), and a diethoxydiaminodiphenylmethane $NH_2(C_2H_5O)C_6H_2\cdot CH_2\cdot C_6H_3(OC_2H_5)NH_2$ from *o*-phenetidine and formaldehyde in presence of hydrochloric acid (D. R. PP. 70402, 72490, 73951, 73946).

Other methods for obtaining 4.4′-diaminodiphenylmethane are (1) the action of *p*-aminobenzyl alcohol on aniline hydrochloride in aqueous solution (D. R. P. 96762), and (2) heating *p*-aminobenzylaniline with hydrochloric acid (D. R. P. 107718)

$$NH_2C_6H_4\cdot CH_2\cdot NHC_6H_5=NH_2C_6H_4\cdot CH_2\cdot C_6H_4NH_2.$$

J. B. C.

DIPHENYLMETHANE COLOURING MATTERS *v.* AURAMINE.

DIPHENYLTOLUQUINOXALINE *v.* AZINES

DIPICOLINIC ACID *v.* BONE OIL.

DIPLOSAL. The salicylic ester of salicylic acid $OH\cdot C_6H_4\cdot COO\cdot C_6H_4\cdot COOH$, a white crystalline powder, m.p. 147°; almost insoluble in water and dilute acids. Used in the treatment of rheumatic diseases (*v.* SYNTHETIC DRUGS).

DIPPEL'S OIL *v.* BONE OIL.

DIPROPYLACETIC ACID *v.* OCTOIC ACIDS.

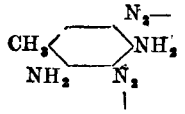
DIPYRIDINE *v.* BONE OIL.

DIPYRIDYL *v.* BONE OIL.

DIRECT BLUE, -BROWN, -GREY, -INDONE BLUE, -ORANGE, -ROSE, -YELLOW *v.* AZO-COLOURING MATTERS.

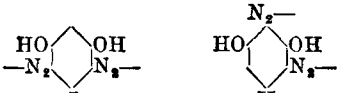
DISAZO- and TETRAZO- COLOURING MATTERS. The terms 'disazo' and 'tetrazo' are both used to indicate the presence of two azo- groups (·N:N·) in the molecule of a colouring matter, but at the same time they indicate the mode of preparation of such dyestuffs rather than, strictly speaking, their constitution. Tetrazo- colouring matters may be regarded as a special division of the disazo-colouring matters, as will be seen from the following classification.

Primary disazo-colouring matters are obtained by the action of two molecules of a diazo- compound (derived either from two molecules of an amine or from two different amines) on one molecule of an amine (*e.g.* *m*-phenylenediamine, *m*-tolylenediamine), a phenol (*e.g.* phenol, resorcinol, a dihydroxynaphthalene) or an aminophenol (*e.g.* aminonaphtholsulphonic acids). The position taken up by the diazo- groups may be illustrated by the commonest cases (*see also* AZO- COLOURING MATTERS). *m-Phenylenediamine:* The azo- groups occupy the two positions para- with respect to the two amino- groups. When one of these para- positions is occupied, as in *m-tolylenediamine*, the second azo- group enters the ortho- position with respect to the second amino- group; thus:



Phenol, α-naphthol. The para- and ortho-positions with respect to the hydroxy- group are occupied.

Resorcinol. Two isomeric disazo- dyestuffs may be formed. When the combination is effected in alkali hydroxide solution, the symmetrical compound (I.) is obtained, but when



I. II.

the reaction takes place in the presence of sodium acetate or sodium carbonate, the unsymmetrical compound (II.) is produced.

Dihydroxynaphthalene. Here the azo- groups enter the usual position with respect to the hydroxy- groups, as would be expected if these groups represented two independent naphthols (*cf.* AZO- COLOURING MATTERS).

Aminonaphtholsulphonic acids. In this case also, the compound may be regarded both as an independent naphthylamine and as a naphthol; one molecule of the diazo- compound is combined in acid solution, when the position taken up by the azo- group is the same as if the substance were a naphthylamine, and the second molecule is combined in alkaline solution as if the substance were a naphthol.

Secondary disazo- colouring matters are obtained by the action of a diazoazo- compound on an amine or phenol; their general formula is $X{\cdot}N_2{\cdot}Y{\cdot}N_2{\cdot}Z$, the essential difference from the primary class being that Y does not contain auxochrome groups (NH_2 or OH).

Tetrazo- colouring matters are produced from diamines, both amino- groups of which are diazotised (*i.e.* the diamine is tetrazotised) and combined with two molecules of the same or different components (amines or phenols). These are mostly derived from benzidine, tolidine, dianisidine, &c.; some, however, are prepared from *p*-phenylenediamine, and in this case direct tetrazotisation cannot conveniently be effected, but the monoacetyl compound is first diazotised and combined, the acetyl- group being then eliminated and the free amino- group is diazotised and combined with the second molecule of a component.[1] When the first combination has been effected with an amine (in practice nearly always a naphthalene derivative), and in consequence a diamino- compound is produced on saponification, treatment with one molecule of nitrous acid leads to the diazotisation of the benzenoid amino- group, that attached to the naphthalene ring not being attacked.

For the sake of completeness, it is necessary here to describe those dyestuffs which contain three or more azo- groups.

Trisazo- colouring matters are obtained in the following ways. (1) Combination of three molecules of a diazo- compound with a phenol. This method is of only theoretical importance, and has hitherto been applied only to the cases of phenol (Wallach and Fischer, Ber. 1882, 15, 2814; Grandmougin and Freimann, *ibid.* 1907, 40, 2662; J. pr. Chem. 1908, [ii.] 78, 384; Heller and Nötzel, *ibid.* 1907, [ii.] 76, 58; Heller, *ibid.* 77, 189), phloroglucinol (A. G. Perkin, Chem. Soc. Trans. 1897, 71, 1154), and resorcinol (Orndorff and Ray, Ber. 1907, 40, 3212; Amer. Chem. J. 1910, 44, 1). (2) Combination of one molecule of a diazoazo- and a diazo- compound with a phenol, amine, or aminophenol. The diazoazo- compound may be produced, for example, by diazotising an aminoazo- compound such as *p*-sulphobenzeneazo-α-naphthylamine, or the intermediate product, obtained by combining a tetrazotised diamine (benzidine, &c.) with one molecule only of a component (such as salicylic acid, &c.), may be used. (3) Combination of a diazotised tetrazo- colouring matter (which must, of course, contain a diazotisable amino- group) with a phenol or amine, either in substance or on the fibre. (4) Combination of a triamine (*e.g.* magenta), having each amino- group diazotised, with three molecules of a component.

Tetrakisazo- colouring matters, containing four azo- groups, are obtained (1) by the combination of two molecules of a diazoazo- compound with a phenol or amine (*e.g.* Mekong yellow, *v.* AZO- COLOURING MATTERS); (2) by combining two molecules of a diazo- compound with one of a tetrazo- colouring matter (*e.g.* Benzo brown G); (3) by combining a tetrazo- compound with two molecules of a monoazo- colouring matter (*e.g.* Hessian brown BB); (4) by tetrazotising a tetrazo- colouring matter (containing two diazotisable amino- groups) and combining with two molecules of a component (*e.g.* Cuba black); (5) by diazotising a trisazo- colouring matter (containing one diazotisable amino- group) and combining with a phenol or amine either in substance or on the fibre.

Colouring matters, containing more than four azo- groups, can be prepared, but, generally speaking, their tinctorial power is little or no greater than those described above. J. C. C.

DISINFECTANTS. A disinfectant is an agent that will kill lower organisms which act injuriously on the higher forms of life. Although most disinfectants are also antiseptics and deodorants, a clear difference between the three classes lies primarily in their uses and objects. Disinfectants are germicides; antiseptics may only retard or inhibit the growths. It is not essential for a disinfectant to effect absolute sterility: in practical disinfection, there is nearly always a residue of highly resistant and non-pathogenic organisms. To destroy these involves great additional time and cost, and may even be disadvantageous when they act as natural scavengers in removing objectionable organic matter and antagonising dangerous forms. The choice of an agent will obviously depend on considerations of safety, convenience, and economy in use.

Ordinary oxygen acts slowly by the aid of aërobic organisms. Its activity is slightly increased by compression; it becomes exceedingly energetic when converted into its allotropic form of **Ozone** as obtained by passing an

[1] An alternative method is first to combine diazotised *p*-nitroaniline with the component, then to reduce the nitro- group with sodium sulphide, and diazotise the amino- group thus formed.

electric discharge through ordinary air. Since ozone is decomposed by heat and absorbed by most metals and by otherwise inert organic matter, the chief conditions for success and economy in working are (1) avoidance of sparking; (2) keeping the gas and the apparatus cool; (3) straining the air, and also partially drying when it is desired to prevent the formation of oxides of nitrogen; (4) parts in contact with ozone must be made of, or lined with, unoxidisable materials; (5) the grosser organic impurities, as well as sulphuretted hydrogen and ferrous iron, should be removed before disinfection. The use of ozone on the large scale for purifying water and sewage is now well known, and the principal types of apparatus for the purpose have been described by Don (Inst. Mechan. Engineers, Jan. and Feb. 1909), and by the writer (J. R. San. Inst. 30, 1, 1909), while a good account of European and American plants is also given in the Engineering News, New York, April 28, 1910. Rideal found at St. Maur Waterworks, Paris, that with the sand-filtered (Marne) river water, containing a fluctuating number of bacteria, 28 to 320 per c.c., with a mean frequency of *coli* organisms of 1 per 100 c.c. (in more than one-third of the tests it was 1 in 40 c.c.), ozone in the proportion of about 0·6 gram per cubic metre of water (6 lbs. per million gallons) destroyed all bacteria except an average of 1 per c.c. of innocuous spore-bearing organisms of the *subtilis* type. The ozonised air was applied in a De Frise tower at the rate of about 40 p.c. of the volume of water treated, and contained 1·4–1·8 grams of ozone per cubic metre (determined at frequent intervals by neutral potassium iodide). It is a great advantage of ozone that in disinfecting the water it produces no alteration beyond a great physical and chemical improvement, and it has been fully proved that where water is not too contaminated with organic matter, sulphuretted hydrogen, or ferrous iron, ozone will destroy all pathogenic organisms at a reasonable cost. In the dry state, like chlorine, it has very little action on micro-organisms, and therefore does not act powerfully on bacilli in air. Some American experiments, however, seem to show that 8 grams per cubic metre of air in a room ordinarily closed accomplish disinfection in 3 hours. Its use as an adjunct to ventilation has often been proposed, but its irritant action on the lungs is a difficulty. All observers have found that when moist it is a very powerful germicide. Ozonised air, under pressure, has been used successfully for destroying moulds and bacteria in brewers' foul casks, and has been introduced into wort in the latter part of the fermentation 'to destroy noxious germs' (Eng. Pat. 22355, 1898). On account of its rapid consumption by oxidisable substances, it can only be effective in disinfecting the *surfaces* of organic solids. At the Pittsburg Homœopathic Hospital, ozone, besides purifying the water supply, is used for sterilising instruments, bandages, &c., and for dressing wounds and ulcers. In cold storage it would probably be useful for destroying injurious organisms and odours, thereby possibly lessening the amount of refrigeration required. Many attempts have been made to utilise it for disinfecting, combined with bleaching, textiles, feathers, and other surface-contaminated articles, and have been only limited by questions of expense.

Patent 4153 of 1902, for 'fixing ozone in liquids,' states that pure acetaldehyde dissolves 2823 times its volume of ozone; that 10 p.c. solutions of acetaldehyde in water dissolve 536, in alcohol 748, in ether 859 volumes of ozone; that these solutions are very stable, and have been successfully used in surgery.

Hydrogen peroxide. The first experiments (Ber. 15, 1585) showed that this was a bactericide which, in the dilute state, appeared inert to enzymes such as diastase,[1] ptyalin, pepsin, and pancreatin; did not injure foods; and is also innocuous and non-corrosive. These properties suggested its use for killing pathogenic organisms, and those that cause change in articles of diet, especially milk (Renard), and also as an internal disinfectant. Altehoefer (Centr. Bakt. 1890, viii. 129) and most later observers give 1 per 100 of H_2O_2 as required to destroy pathogenic organisms in 24 hours. In 1903 the writer found that in milk raised to 50°, then treated with 0·6 gram of H_2O_2 per litre, and the heat maintained at 52°–55° for 8 hours, pathogenic organisms and even the spores of *B. anthracis* and *subtilis* were killed, the milk was not physically altered, and kept for over a month unchanged in the closed receptacles (Budde's patent 10903, 1903). Similar results have been obtained by Lewin and others, and by Hewlett (Lancet, Jan. 27, 1906). So that hydrogen peroxide aids pasteurisation, and enables it to be efficient at a lower temperature. The solution is frequently used as a spray, gargle, or dressing. Peroxide of hydrogen is present in 'Sanitas' (*q.v.*). 'Perhydrol' is a 30 p.c. or 100 volume solution of H_2O_2. The use of peroxide of hydrogen in medicine depends partly on its bactericidal action. Registered names of solutions are 'Dioxogen' (3 p.c.), 'Hydrozone,' 'Glycozone' and 'Pyrozone' (dental practice); and 'Peroxols' are mixtures of H_2O_2 with various disinfectants. Peroxides of sodium, magnesium ('Hopogan'), zinc ('Ektogan' or 'Dermogen') and mercury, generate oxygen or H_2O_2, and have analogous use. Hydrogen peroxide is more stable in ether than in water; 'ozonic ether' is an ethereal solution containing about 1·2 p.c. of H_2O_2, which has been used in whooping-cough and scarlet fever.

Foregger and Philipp (J. Soc. Chem. Ind. 1906, 298) treat at length on the applications of peroxides, and suggest calcium peroxide instead of H_2O_2 for sterilising milk, as more lasting in effect. For water sterilising, tablets of magnesium peroxide and citric acid are made; Park found that 0·1 gram of this peroxide killed upwards of 2 million typhoid organisms in 150 c.c. of water in 30 minutes, and 0·2 gram gave the same result in 1 minute. Patents for similar uses of H_2O_2 and other peroxides are very numerous.

Nitric acid and oxides of nitrogen. The corrosive action of nitric acid limits its value as an active disinfectant. J. C. Smith used it with success in 1780 for fumigation in a violent

[1] The enzyme *catalase* (present in malt, yeast, milk, and many organic liquids) and hydrogen peroxide mutually decompose one another (Van Laer, J. Soc. Chem. Ind. 1906, 489; 1909, 950); but the above statement remains practically true. (*See also ibid.* 1909, 1267.)

outbreak of *typhus* fever in the British fleet (Vallin, Désinfectants, 1882, 265). Disinfection of rooms by nitrogen peroxide was carried out during the siege of Paris; 48 hours were occupied, and the cost was very high. Severe bronchitis and several deaths from poisoning have resulted from breathing this gas, and nitric disinfection has been replaced by safer methods, except in the local destruction of bacteria as in laboratories.

Sulphur. Dusting with sulphur is used for killing insects and fungi on plants, as sulphurous acid is gradually formed. The use of sulphur internally is due to its forming sulphuretted hydrogen in the system, and thereby destroying or enfeebling micro-organisms and higher parasites. A solution containing calcium polysulphides, made by boiling milk of lime with sulphur, has been extensively used as an insecticide (*see* Agric. Bull. 319 and 320, New York, 1909).

Sulphur dioxide disinfection is still a subject of controversy, but certain of the unfavourable results adduced have been due to faulty application. Spores are not generally killed by it, and the dry gas has very little effect on micro-organisms, but it destroys all vermin, and therefore is of special value in combating insect-borne diseases. As to its effect on the lungs, about 5 p.c. in the air has produced fatal results, but ½ p.c. can be tolerated for some time, and a larger amount with the protection of a wet towel alkalised with washing soda. 1 lb. of sulphur burnt in a room of 1000 cubic feet produces theoretically an air-content of 1·15 p.c. SO_2, and requires 0·56 lb. of water to turn it into sulphurous acid. Such an amount of moistening is, however, not necessary, on account of the natural moisture of the air. Prescriptions as to the proper quantity of SO_2 have varied greatly, partly because in some cases it has been considered sufficient to destroy only a special organism. Klein, Houston, and Gordon (Report, Med. Off. L.C.C. 1902) found that with 3½ lbs. S per 1000 cubic feet in 24 hours, *B. typhosus, diphtheriæ, pyocyaneus,* and *Staph. p. aureus* were killed, but not anthrax spores nor *B. tuberculosis* in dried sputum. In America, 5 lbs. per 1000 cub. feet have been found sufficient to kill all spore-bearing organisms after 16 hours' exposure (Rosenau). Rideal's results with the liquefied gas were as follows. Silk threads and paper slips infected with *B. coli* and *Staph. p. aureus* were sterilised after 24 hours' exposure in a sealed room of 1500 cub. feet, into which 20 ozs. of SO_2 were passed. *Subtilis* spores were not killed. With 10 ozs., the threads were again sterilised, but the paper slips were not. When shallow pans of water were exposed in the room to supply moisture, the SO_2 content of the air was actually *lowered* after the 24 hours (through absorption by the water), from 0·5 p.c. present in the previous experiment to 0·2 p.c., and the organisms were still living. Therefore moisture should only be supplied by washing or lightly spraying the surfaces. In chemical disinfection, it is generally recommended that walls should be previously stripped and fabrics spread out in lines; but spreading the infection must be carefully avoided. The room must be sealed by obvious means, and, observing this condition, heating is advantageous. Liquid SO_2 in canisters is more convenient than burning sulphur, and avoids risk of fire: one pound of the liquid = 5½ cub. feet of the gas. SO_2 has the disadvantage that it attacks metals and organic substances from the production of sulphuric acid; a good deal is also absorbed by plaster. It has little penetrating power, and therefore bedding and thick articles must be removed and sterilised by heat. The 'Clayton method' of disinfection is much used for the holds of ships, and has been favourably reported on by Wade and Eyre for the Local Government Board (Rep. 232, 1906; and Med. Off. Rep. 1903–4, 330). Sulphur is burnt in a special apparatus, and the gases, consisting of air, SO_2, and a visible cloud of sulphuric acid, are forced in till the SO_2 reaches about 10 p.c. of the air in the infected space. (For experience of its use, *see* Rev. d'Hyg. Oct. 1902; N.S.W. Agric. Gaz, 1900 and 1901.)

Sulphurous acid is used beneficially as a germicidal spray or wash in various parasitic affections (*e.g.* diphtheria), also internally in cholera and gastric fermentation, for rectal injections, and other allied objects. 'Thiocamf' is a liquid obtained by the action of the gas on camphor. It can be preserved without pressure in well-closed vessels, and on exposure to air a 6-oz. bottle should evolve about 20 litres of SO_2.

Sulphurous acid and bisulphites are widely used for checking fermentations and preserving food. Lehmann states that an amount equivalent to 0·004 p.c. of SO_2 may be allowed without injury to health. The Report of the British Departmental Committee on Preservatives, 1901, 26, leaves the matter open. Some commercial preparations are 'Meat preserve crystals,' 'Freeze-em,' and 'Hawke's antiferment.' For objections to the use of sulphites in food, *see* Thresh and Porter, Preservatives, 1906, 70–77; also an article by Durham in the J. of Hygiene, April, 1909. The latter recommends the fixing of a maximum legal limit, not exceeding 0·01 p.c. of 'total sulphur dioxide,' with a declaration of the amount, but less than 0·001 or 0·002 p.c. might be simply declared as a 'trace.'

Sulphuric acid, like acids generally, is antiseptic, and in some cases disinfectant. 0·05 p.c. (which is a palatable strength) is fatal to *Sp. choleræ* in 15 minutes. Stutzer found that this strength disinfected iron pipes, cleaning out rust and sediment without sensibly attacking the metal. With 0·04 p.c. Ivanhoff destroyed cholera organisms in Berlin sewage, and with 0·08 p.c. in that from Potsdam. The writer finds that 0·035 p.c. kills *B. typhosus* in 30 minutes, and 0·07 p.c. in 15 minutes, in impure water infected ordinarily with typhoid, but with very heavy infections the latter strength requires 45 minutes. He recommended 0·09 p.c. as having advantages over heat sterilisation for dealing with the drainage from hospitals and other infected areas: the acidity would speedily be neutralised on mixing with the bulk of the sewage (Brit. Assoc. 1901).

Sodium bisulphate has been introduced by the writer and Dr. Parkes, as a means of sterilising drinking water for armies in the field and travellers. 15 grains of $NaHSO_4$ to a pint of water in 15 minutes destroys *B. typhosus* and *enteritidis, Spirillum choleræ,* and internal

parasitic worms. In effervescent tabloids, yielding a slightly acid solution, it was used with success in the South African and Russo-Japanese wars.

Persulphates give off oxygen when moist, and are useful as hand disinfectants (Lancet, 1905, ii. 1106).

Carbon disulphide, if it were not for its other properties, would be a valuable disinfectant and preservative. As well as its alkaline compounds, the xanthates, it has been found useful against fungi, and insect parasites such as the vine phylloxera. Ckeandi Bey's lamp burns it safely for generating SO_2.

Boric acid is not a disinfectant, but has a power of restraining bacteria which act injuriously in foods. Rideal and Foulerton found that 1 in 2000 of a boric mixture, containing 3 parts of H_3BO_3 and 1 part of crystallised borax, keeps milk sweet for 24 hours without appreciable effect on digestion. The British Departmental Committee already referred to, recommend that the only preservatives allowed to be used in cream, butter, and margarine be boric acid, or mixtures of boric acid and borax, not exceeding 0·25 p.c. of H_3BO_3 for cream, and 0·5 p.c. for butter and margarine. Later, as this quantity appeared insufficient in the cream trade, an official report by Hamill advised that 0·4 p.c. H_3BO_3 should be allowed in cream from May to October inclusive (Food Report 10, L.G.B. 1909).

The Halogens, chlorine, bromine, and iodine, act as disinfectants in several ways: (1) they can combine with H and liberate O in water; (2) they can combine directly with organic matters, or replace the hydrogen in them, precipitating albuminous substances and rendering them imputrescible, killing organisms by combining with and coagulating protoplasm, removing their food or rendering it unsuitable, acting toward them as irritants or direct poisons, also producing substances which have that effect.

Chlorine and the hypochlorites, like other oxidisers, are consumed by otherwise inert organic and inorganic matters present, but in ordinary disinfection leave behind them as substitution compounds which maintain germicidal power—the chloramines, hydrazine, and the chloroproteids (Rideal, J. R. San. Inst. 31, 2, 1910). This paper shows that in dilute solution the Rideal-Walker coefficient of 2·18 for 1 p.c. of available Cl is increased to 6·36 by the addition of an equivalent of ammonia, remains near this level for 24 hours, and even after 72 hours has an enhanced value. Therefore, since the coefficient of chlorine itself averages 220 units, that of ammonia less than 0·7, and ammonium chloride *nil*, that of the chief product, *chloramine* NH_2Cl, must be over 600 units; hence this substance, but for its instability, would probably be the most valuable of disinfectants. It has a pungent odour, hitherto often mistaken for chlorine or hypochlorous acid, and gives the blue reaction with KI and starch. With excess of ammonia, as in sewages, it gradually disappears, forming a salt of *hydrazine*, which still has a germicidal value (R. W. coefficient of the base at least 24). The action of chlorine on nitrogenous compounds gives compound chloramines, many of which are insoluble: they have a tendency to become fixed on cellulose, and in this way attack the envelopes of organisms.[1]

Chlorine in the free state has been generally disused in disinfection on account of difficulties in practice. Hypochlorite preparations must be tested as to the amount of 'available chlorine.'

Chloride of lime, or 'calx chlorinata' (about 33 p.c. available chlorine), has some advantages from being a solid, but is quickly deliquesced and decomposed by air, takes some time to dissolve, and gives a quantity of insoluble waste. Klein found that 1 p.c. of bleaching powder only killed less resistant organisms in 24 hours. There is, in many respects, a preference for the sodium solutions: chlorinated soda or 'Eau de Labarraque' (often called 'Eau de Javel,' which was originally the potash salt), contains about 2·5 p.c. av. Cl; 'Chloros,' 10 p.c. av. Cl; 'Antiformin' is a solution of caustic soda and hypochlorite used in breweries. Electrolytic preparations are 'Oxychloride,' up to 11·5 p.c. av. Cl, and 'Hermite fluid,' used successfully at Poplar. In the latter solution magnesia is employed as an adjunct in the electrolysis: it contains free hypochlorous acid: av. Cl 4·2 to 4·8 p.c. The electrolytic are somewhat more active than the chemically prepared solutions. The effective strength for local disinfection is 0·35 p.c. av. Cl, which kills non-sporing organisms in 5 to 10 minutes, and anthrax and enteritidis spores in 1½ hours. Chloride of lime has the objection that it leaves the surface for a long time damp from the presence of calcium chloride. The same salt imparts its bitter taste, and increases the hardness, when chloride of lime is applied to the purification of drinking water, while the soda preparations tend to soften the water and are not sensible in the flavour. In trials at Guildford in 1904 (J. R. San. Inst. xxvi. 891) with electrolytic hypochlorite in the proportion of 0·75 to 1·0 part per million of av. Cl, the writer found that water containing an average of 90 organisms per c.c. was practically sterilised, while after standing 1½ hours the odour and taste were normal, and there was no need for further treatment. (Candy's patent, 4212, 1909, removes excess of av. Cl by filtration through coke, and Thresh's, 3023, 1909, by treatment with metallic iron.) After the Maidstone typhoid epidemic, 1897, the infected reservoir, mains, and pipes, were sterilised with 1 p.c. solution of chloride of lime during 48 hours: no corrosion of the iron was observed. During a similar outbreak at Lincoln, in 1905, the water supply was sterilised by sodium hypochlorite (av. Cl, 1 per million) with most satisfactory results. In 1910 Toronto treated its water supply with 0·14 part per million of av. Cl as chloride of lime. Since June, 1909, the writer has been applying 'Chloros' in the proportion of 1 to 2 parts av. Cl per million to 100,000 gallons daily of the drinking water of a town in the north of England: the liquid is made practically sterile, *coli* is absent from 75 to 85 c.c., and there is no effect on the taste. At Cambridge, in 1910, a portion of the supply (lower chalk) was treated with one in 4 to 8 millions of av. Cl as chloride of lime, and Houston found that this minute quantity destroyed 66 to 98 p.c. of the bacteria, and *coli*, which was always present

[1] Also see Cross Bevan and Bacon, Chem. Soc. Trans. 1910, 244.

before, was afterwards absent in 500 c.c. This water, however, contained hardly any organic matter. In America, treatment of the entire water supply of Jersey City (about 40 million gallons per day, from the Rockaway river) with chloride of lime, has been adopted since the beginning of 1909: the proportion used is now 0·2 part per million of av. Cl, and the daily examination shows that *coli* is absent from 10 c.c. of the treated water.[1]

With sewage, of course, a larger dose is required, and the first experiments at Nice, Brest, and Worthing, in 1894, with the Hermite fluid, showed that, as with ozone and other disinfectants, the agent should be applied, not to a raw liquid (except in special cases), but as a 'finisher' to one that was partially purified. In 1898, using an electrolytic brine (Woolf's 'Electrozone') for purifying an effluent at Maidenhead, the writer found that with three parts per million of av. Cl, and a contact of 5 minutes, the bacteria were reduced to 10 per 50 c.c., and that 17 parts per million killed all the organisms in 15 minutes. His long series of trials at Guildford commenced in 1904, using 'Oxychloride,' and proved that with 2·5 parts per million of av. Cl, tertiary effluents could be practically sterilised, but that the raw sewage and septic effluents required 30 to 70 parts; the contact period was 4½ hours (J. R. San. Inst. xxvi. 7, 1905). The oxygen consumed from permanganate in 5 minutes in the cold, as measuring the H_2S and other easily oxidisable substances, was a guide to the amount of the agent used, and in the earlier experiments it was found that when the av. Cl added was 1·7 times this figure, the availability of the chlorine was sufficiently prolonged to ensure the desired sterilising effect, and the subsequent experiments frequently yielded excellent results with an amount *equal* to this oxygen figure, that is, one to one. (*See* further, Rideal, Trans. Farad. Soc. iv. 3, 1909.) An important point shown was that the necessary factor of safety could be ascertained by simply testing with KI and starch, and noticing the persistence after 4½ hours of the blue colour, due in this case, as has been mentioned, not to chlorine, but to chloramines. Schumacher used the test similarly in his later extensive experiments on *raw* sewages (especially those from hospitals) at Hamburg, and states that with them sufficient sterilisation is attained if after 4 or 6 hours the test shows a reaction equal to 19 and 17 parts per million of av. Cl respectively (Ges. Ingenieur, Berlin, 1905). Investigations on the sterilisation of sewage filter effluents with chloride of lime were continued in America by Phelps and Carpenter (U.S. Technological Quarterly, Dec. 1906), who remark that the use of electrolytic chlorine manufactured on the spot would, in the larger works, considerably reduce the cost, and is cheaper than sand filtration, and Kellerman, Pratt, and Kimberley (U.S. Dept. of Agric. Bull. 115, Oct. 1907), who conclude that with a hypochlorite, complete disinfection was effected at a lower cost than with copper sulphate. Later American experiments at several centres have proved that 2 to 5 parts per million of av. Cl destroy 95 to 98 p.c. of the bacteria in 2 hours, and that 3 parts are sufficient for the trickling filter effluents tried (Mass. Inst. Technol. 5, 1909; 6, 1910).

The Royal Commission on Sewage obtained results at Guildford which were in agreement with those of the writer (Appendix iv. 1910, 87; also *ibid.* 84–171, and Rep. 1908, 195–201).

Sod. hypochlorite solutions are the best means of sterilising swimming baths; they remove from the surfaces growths of algæ and fungi which harbour dangerous organisms. (*Also see* Rideal and Orchard, J. San. Inst. 556, 1906.)

'Ferrochlore' (Duyck) is the name of a treatment with 8 parts per million of ferric chloride and 0·5 part of chloride of lime, which at the same time clarifies water and liberates hypochlorous acid.[1]

Chlorine peroxide, obtained from potassium chlorate and sulphuric acid, has been successfully employed in the Howatson-Bergé process at Brussels, Ostend, and Lectoure (South France), for sterilising (previously clarified) polluted waters. The writer found that 20 parts of ClO_2 per million did not kill *B. typhosus* in a vigorous pure culture in 2 hours, but that 50 parts killed it in half an hour. (*See also* Reychler, Bull. Soc. chim. [3] xxv. 13; Chem. News, 1901, 316.)

On a large scale, chlorine and ozone are both in successful use at present for sterilising water. The latter seems preferable for drinking supplies, the former is suitable for effluents. From questions of efficiency as well as cost, both require that the liquid should be clear or previously clarified, that is, they are *finishers*. In potable waters, on account of the liability to persistence of Cl, several dechlorinating devices have been employed, as mentioned above.

Time, as in all disinfections, is an important factor; in an effort to get the work done quickly, it is sometimes forgotten that a longer time is advantageous, and economises the reagent. For rapid sterilisation of a small quantity, as in the field, a larger proportion of reagent is required, and from questions of portability, bromine and iodine have been used instead of chlorine, but are attended by residual products having a taste and physiological effect. These, in the quantity required for dealing with the moderate pollution ordinarily met with, have been proved to be negligible, although, with heavier contamination, the amount of the halogen consumed by the organic matter before a sterilising excess is present, may become injurious in its products. Cash, from experiments on anthrax and tubercle, maintained that the quantities of chlorine, bromine, and iodine required for disinfection under the same circumstances were nearly in the ratio of their atomic weights (*see* R. W. table at end of article). Iodine is, however, a more immediate poison to protoplasm than chlorine.

Bromine is a powerful disinfectant, but its use is obviously limited by its danger: In 1897 Altmann patented a solution of Br in KBr for sterilising water, using 40 parts per million of Br with 5 minutes' contact, and removing excess

[1] In England, the 'De-Chlor' system is applied at Reading to the prefiltered river water (Surveyor, Dec. 16th, 1910). At Antwerp 0·2 av. Cl per million is added to the storage reservoirs, with a contact of 12 hours.

[1] For an account of trials at Marseilles of ozone, chlorine, and ultra-violet rays, *see* Engineering, Jan. 27th and Feb. 3rd, 1911.

by ammonia. The solution is, however, bulky, and the use of a potassium salt has disadvantages. Braithwaite introduced 'Bromidine,' a dry mixture of sodium or potassium bromide and bromate with sodium bisulphate, which with moisture liberates bromine. Schumberg recommended free bromine in thin sealed tubes for the same purpose (Zeitsch. f. Hyg. 1900, 53) in the proportion of 60 parts per million with 5 minutes' contact, removing excess by thiosulphate (Braithwaite advised 57 parts). Schöder (*ibid.* xxxvii. 306) and others have stated that this treatment is insufficient to sterilise, and the presence of residual bromides is against the process (*see also* Parkes and Rideal, Trans. Epidem. Soc. xx. 1901; Fraser, Publ. Health, Sept. 1902). It was tried in the Soudan campaign of 1898. The writer found that 20 parts per million of Br sterilised *typhosus* (in water) in less than half an hour. It is more rapidly absorped by organic matter than iodine.

Iodine owes many of its uses to its germicidal action, as in parasitic diseases. Grossich, in 1908 (Centr. f. Chirurg. No. 4), adopted the tincture as a cutaneous disinfectant before operations, the surface being previously cleansed by a 1 p.c. solution of iodine in benzene (Bogden, *ibid.* Jan. 15, 1910). Instead of the tincture, Chassevant (Lancet, March 26, 1910) suggests the solution in chloroform, as it does not, like the former, cause desquamation; its use is specially advised prior to hypodermic injections (*see also* Brit. Med. J. Feb. 6, 1909, and Aug. 14, 1910; Lancet, April 16, 1910). During the Sikkim and Thibet expedition, iodine (in some cases as tincture) followed by sodium sulphite, was successfully employed for sterilising drinking water, and Nesfield recommends triple tablets of (A) iodide and iodate, (B) citric or tartaric acid, followed after 2 minutes' contact by (C) sodium sulphite, and states that used in this way 3·8 to 5 parts per million of free iodine sterilises the organisms of typhoid, cholera, and dysentery. The writer, in 1905, confirmed this result as regards distilled water infected with 20,000 per c.c. of *B. typhosus*, the A and B tablets used gave 4·75 parts of iodine per million.

Iodine trichloride was introduced by Von Langenbach for sterilising the hands and instruments and for other surgical uses. The writer finds that 50 parts per million are required to kill typhoid (in water) in 30 minutes. Iodine cyanide is said, by Kobert, to be universally destructive to lower forms of life, and is suggested for preserving biological specimens.

Organic substitution compounds of chlorine, bromine, and iodine, as a class, inhibit organisms, and may sometimes kill them. The germicidal power of a large number of these has been determined by Bechhold (Zeitsch. Hyg. Infect. 1909, lxiv. 113): he finds that a Br atom gives a greater power than a sulphonic group. *Chloroform* is often used to preserve perishable specimens and infusions. Farrel and Howles (J. Soc. Dyers, 1908, 24, 109) state that CCl_4 kills typhoid, and that pure $CHCl_3$ does not kill it, whilst 0·62p.c. aqueous $CHCl_3$ kills it in less than 30 minutes.

Iodoform was formerly much employed in surgery, and a large number of other iodine compounds have been introduced into medical and surgical practice. Many of them are non-irritant, but their bactericidal power is much inferior to that of dilute solutions of the element. Fumigation of sick rooms with iodine, sometimes in conjunction with other disinfectants, by burning prepared candles or lamps, has been tried, but apart from the fact that the method is unsatisfactory, no chamber can be disinfected while occupied.

Fluorides, like boric acid, check bacteria, but do not kill them. As food preservatives, they are only moderately efficient, and are not innocent physiologically, as they hinder pancreatic digestion. Sodium silicofluoride ('salufer') and borofluoride ('pyricit') have been tried. Effront introduced the use of hydrofluoric acid and its acid salts for checking injurious fermentations, and J. Brand (Zeitsch. f. Brauw. 1904, xxvii. 115) states that 0·5 to 1 p.c. solution of acid ammonium fluoride is largely used for disinfecting rubber hose in breweries (*see also* Hehner, Analyst, 1902, 173; Richmond, Dep. Comm. on Preservatives, appendix xxxii.; Thresh and Porter, Preservatives, 1906, 87). Hydrofluosilicic acid is the active constituent of 'Montanin' (obtained from by-products in the pottery industries), and 'Keramyl' (about 25 p.c. H_2SiF_6) (J. Soc. Chem. Ind. 1904, 34; 1909, 904).

Carbonic acid seems to have a certain amount of disinfectant action, since 'aërated' beverages have been shown to be in many cases sterilised, and CO_2 under pressure preserves food (*cf.* J. Soc. Chem. Ind. 1907, 1290).

Cyanogen and hydrocyanic acid are more destructive to insects than to lower organisms. Fumigation of fruit trees with HCN is extensively practised in America, and is considered better than spraying. For greenhouses, zinc capsules containing sodium cyanide are made: they are placed in dilute sulphuric acid, and while the zinc dissolves the operator has time to retire.

Acids. An acid medium is unfavourable to the growth of most bacteria, and acids generally possess considerable disinfectant power. Kitasato found that the growth of *B. typhosus* in nutrient broth or gelatine was entirely prevented by the following percentages of different acids: 0·08 H_2SO_4; 0·2 HCl or HNO_3; 0·28 SO_2; 0·3 to 0·4 phosphoric, acetic, carbolic, formic, oxalic, or lactic; 0·476 tartaric, citric, and malic; 1·66 tannic; and 2·7 boric. The writer has shown that in infected waters, 0·035 p.c. of H_2SO_4 kills typhosus in 30 minutes, that in terms of acidity nitro-hydrochloric was slightly more active, and that with tartaric and citric at least three times the amount of acidity was required (Epidemiological Society, Jan. 1901). But like other disinfectants, the activity of dilute acid solutions is considerably modified by the presence of added matters; for instance, in 1 p.c. peptone broth, *Sp. choleræ* is killed by 0·01 p.c. hydrochloric acid in half an hour, but in 2 p.c. peptone broth, 0·04 p.c. HCl is required.

Paul, Krönig, and Sawey (Pharm. J. 1900) conclude that the germicidal activity of acids generally, depends upon the degree of ionisation in solution, exceptions being HF, HNO_3 and trichloracetic, which exercise specific toxic influences. In normal solutions, the three latter killed anthrax spores exposed on garnets in 24 hours, while H_2SO_4, HCl, HBr and $HClO_3$ were less active. Working with more dilute acid solutions, Winslow

and Lochridge (Mass. Inst. Tech. 1906) have compared the effect on *B. coli* and *typhosus* in tap water and in a 1 p.c. peptone water. With upwards of 10,000 organisms per c.c., sterilisation was obtained by the following percentages of each acid after 40 minutes' contact :—

	B. typhosus		*B. coli*	
	Tap water	1 p.c. peptone water	Tap water	1 p.c. peptone water
Hydrochloric acid	0·018	0·174	0·045	0·368
Sulphuric „	0·022	0·188	0·081	0·530
Acetic „	—	—	0·561	0·836
Benzoic „	0·069	0·292	0·242	0·555

In agreement with the results of other workers, larger amounts of each acid are required to disinfect in the presence of peptone ; with the organic acids, benzoic and acetic, this diminished activity is not so pronounced. Winslow and Lochridge find that the disinfectant power of the acids is not proportional to their strength in terms of normality, but, in the case of the mineral acids, hydrochloric and sulphuric, to the degree of ionisation of the solution, 99 to 100 p.c. reduction of *B. coli* or *typhosus* being effected with either acid at the same concentration of dissociated hydrogen. The evidence tends to show that the alteration in ionisation in a dilute acid solution brought about by the presence of otherwise inert substances in solution, as, for example, neutral salts of the acid, accounts for the variation in germicidal activity. In practical disinfection, the subject is often rendered still more complex by a further interference—the absorptive effect of solids in suspension. Therefore the acidity, as found by titration, does not give the germicidal value of an acid solution unless these disturbing factors are considered.

Metallic derivatives. Warm alkaline leys are the most ancient of disinfectants : potassium and sodium hydroxides are sterilisers in the proportion of not less than 2 to 5 p.c., their carbonates in 5 to 10 p.c. At 60° a contact of 5 minutes ensures the death of most organisms (Zeitsch. f. Hyg. 1903, 349), hence ordinary soaps have a slight disinfectant value. Strong brine is preservative, but not disinfectant, and the practice, formerly frequent, of washing out milk cans and other utensils with it, is not a safe one. Lode shows (Chem. Zentr. 1902, i. 1122) that 50 p.c. salt solution does not kill the spores of common moulds.

Lime, as quicklime, is fatal to bacteria when it comes in contact with them in an almost dry condition, and has been much used where there is a considerable space and bulk of material to be dealt with. It is not safe, however, to trust entirely to the old method of burying infected bodies in lime, as, on disinterring, the live spores may again be diffused, unless a long period has elapsed. The disinfecting power of milk of lime and whitewash has been much overrated ; as to milk of lime, Liborius stated (Zeitsch. f. Hyg. ii. 25) that in the proportion of 74 parts per million of CaO, it destroyed typhoid bacilli, and that 246 parts per million were required for cholera organisms, while 2 p.c. of dry lime was needed for cholera discharges ; with in each case 'a few hours'' contact. When lime is added to sewage, a great number of bacteria are carried down, but are not killed, and the supernatant liquid is not sterilised. *Zinc chloride*, 'Burnett's fluid,' formerly in high repute as a disinfectant, is not reliable in its effect, and ranks below copper sulphate and mercuric chloride. The sulphate has still less energy (R. W. coeff. 0·09).

Aluminium chloride, 'chloralum,' was classed by Miquel between zinc chloride and copper sulphate. *Iron salts*, especially ferrous sulphate, were at one time in vogue for sanitation, but are ineffective.

Permanganates and manganates were first introduced as Condy's red and green fluids. Like oxidisers generally, they are largely consumed by otherwise inert matters before attacking organisms, and as complete disinfection cannot be ensured unless an excess of reagent remains, evidenced by a pink colour, which is not always easily visible owing to the brown oxide of manganese produced, their use may be very costly and its execution frequently imperfect. The writer carried out experiments in street-watering of two similar areas of ordinary soiled asphalt roadway : (*a*) with water alone ; (*b*) with permanganate solution 1 in 5000 (six times the amount then customary), and examined the liquid from the surface. The permanganate was almost immediately decolourised. Sample (*b*) was nearly inodorous, on keeping became much less foul than (*a*), and the reduction in the number of organisms was 96 p.c., but the survivors included a large proportion of the dangerous forms (Rideal's Sewage, 1906, 117). For polluted water Rosenau recommends adding permanganate drop by drop till the pink colour persists for 24 hours. 'Pinking' of wells was many years ago adopted by Hankin in India as a precaution against cholera. Permanganates, used in various ways, are still being patented, chiefly for water purification.

Chromic acid, although a powerful oxidiser and instantly coagulating albumen, is excluded by its cost and poisonous and corrosive nature from the list of useful disinfectants or of preservatives.

Arsenic, like cyanogen, has more effect on higher than on lower forms of life, and is the basis of valuable insecticides, such as the sheep-dip solutions of arsenious oxide or sulphide in soda, frequently associated with tar products and nicotine. *See* Chemist and Druggist, June 11, 1904 ; Rep. Dept. Comm. B. of Agric., leading to the Sheep-Dip Act of 1903 ; and Quibell, J. Soc. Chem. Ind. 1907, 1266. The copper compounds, '*Paris green*' (aceto-arsenite) and others, are used for spraying or dusting trees, combining the actions of arsenic and copper. Several organic arsenic compounds have been introduced as medicinal parasiticides (*see* Lancet, Brit. Med. J., &c., 1910 and onwards).

Some metals in the free state are antagonistic to germs. Dievert states (Compt. rend. 136, 707) that agitation with granulated zinc kills *B. typhosus* and *coli* in a few hours, and Baeyer's method of treating polluted waters with zinc-dust, charcoal, and lime causes, according to Margösches (Leipz. Monats. Textilind. 1901, vi.), practical sterilisation. Rankin (Proc. Roy. Soc. 1910, B, 82, 78) shows that clean strips of Al, Zn, or Cu, in air-free water, do not reduce the number of *coli*, whilst when air is bubbled through there is a great reduction after 1 hour. Except with Cu, peroxide of hydrogen was produced, but the amounts of this and of the metal dissolved

were too small to account for the germicidal effect, which is ascribed to the metal and oxygen together. *Metallic iron* has long been used for purifying water, as in Anderson's process (J. Soc. Arts, Feb. 14, 1896): in this case, galvanic action and the oxides formed come largely into play, but Frankland proved that the metal itself was, to a certain extent, bactericidal. Old Hindoo writings direct water to be kept in vessels of *copper*; among modern observers, Nageli, Galeotti, and Israel and Klingman hold that there is formed a colloidal solution which renders the water toxic to many algæ and bacteria. In 1904 the U.S. Dept. of Agriculture reported that 1 sq. cm. of bright copper per 100 c.c. of water was sufficient to exterminate *Uroglena* and some forms of *Spirogyra*, and Kraemer showed that the same treatment destroyed colon and typhoid bacilli in 4 hours, whilst colloidal copper was quickly fatal to these organisms. For household purification, he commended the use of strips of copper, about 3½ sq. inch to each quart (2 sq. cm. to 100 c.c.), immersed in the water for 6 to 8 hours. In a similar way, Rideal and Baines (*J. San. Inst.* 1904, 594) obtained sterilisation of *typhosus, coli,* and *S. py. aureus* in less than 24 hours. Bassett Smith (J. Prev. Med. July, 1904) found that in a bright copper vessel, *B. typhosus* was still living at 12 hours, but was dead at 24, and that of ordinary water organisms, 1020 per c.c. at first, only 8 per c.c. (none of them liquefying) were left after 24 hours. He concluded that clean iron or zinc was nearly equal to copper in first effect, but soon lost the power by oxidation.

Copper salts have a distinctly poisonous action on lower organisms, partly from their coagulating albumen and combining with many of the constituents of the tissues. Kroncke considered *cuprous chloride* to be the most active of the salts: he treated Elbe water, containing 40 to 50 thousand organisms per c.c., with 50 parts per million of Cu_2Cl_2 and 20 parts of ferrous sulphate, allowed 6 hours' contact, then agitated with 10 parts of lime. After settling and filtration through sand, the water was sterilised, clear, and colourless, and free from iron and copper. Schumberg (Chem. Zentr. 1900, ii. 203) corroborated the sterility at the end of 6 hours. The efficiency of soluble cupric salts is generally dependent on their percentage of copper (Green, Zeitsch. f. Hyg. 1893, 495; Rideal and Baines, *l.c.*), but the sulphate is commonly used as most convenient. For disinfecting sewage effluents (and inferentially for reservoirs), American investigations conclude that copper sulphate 'is not so efficient as chlorine compounds, is more seriously affected by carbonates, and is much more expensive' (U.S. Geol. Survey, Water Supply Paper 229, 1909, 32; *also see* Bull. U.S. Dept. of Agric. No. 100, 1906).

Disinfection of excreta and morbid products, even with considerable quantities of copper salts (*e.g.* 5 to 10 p.c. of the sulphate), is not reliable. For killing agricultural parasites, their use is well known, including that of the sulphate for soaking seeds and against potato blight, also verdigris (acetate), 'Paris green' (arsenite), copper-lime-sugar and copper-soap washes for trees, and 'Bordeaux mixture' (copper sulphate and lime). The last named was introduced for vines, but has been since extended to other crops. In reference to the general practice of employing the metallic compound in the precipitated or solid form, instead of in solution, the main points stated are (1) that, in the former way, it is not liable to injure the plant or contaminate its tissues; (2) that the copper should remain as an external coating, because the spores germinate on the surface; (3) that uncertainty of composition and inequality of application are overcome by certain precautions and definite prescriptions. *See* British Board of Agriculture leaflets 23 and 225: the latter (May, 1909) gives a method of preparing and using Bordeaux mixture: 'for a 3 p.c. solution, 3 lb. copper sulphate and 2 lb. freshly burnt quicklime to 10 gallons of water.' *See also* J. Soc. Chem. Ind. 1896, 332; 1907, 1291; Compt. rend. 1911, 152, 532. Chuard (*ibid.* 1910, 150, 839), estimating that 12,000 tons of copper are thus consumed annually in France, expresses anxiety as to the result of its accumulation in the surface soil, and with a view to reducing the quantity states that a half p.c. aqueous mixture of the oxychloride is as adhesive and effective as the usual 2 p.c. paste of the sulphate. Cupric sulphate impregnation for preserving or 'kyanising' timber has been superseded by creosote oils, since the former washed out of the wood. 'Microsol,' sold as a soluble disinfectant for stables and drains, contained 75 p.c. of copper sulphate with sulphocarbolate and some free sulphur dioxide.

Mercury.—Mercuric chloride, 'corrosive sublimate,' has long been recognised as one of the most powerful of disinfectants, and a 1 per 1000 solution was the earliest standard for comparisons. Apart from cost, points limiting its utility to special purposes are: (1) the poisonous effect on higher animals and plants; (2) its precipitation by so large a number of substances, such as hard water, alkalis, and numerous salts, metals, sulphides, and many organic bodies, causing its action to be liable to great variations and inconveniences. It will often form a pellicle over organisms without killing them, and it is inapplicable to the disinfection of sputum, excreta, and the like, from its producing a coagulum which prevents further penetration. Sodium or ammonium chloride is sometimes added to increase the stability of the aqueous solution, but considerably diminishes the germicidal power. The Local Government Board recommended for disinfecting purposes: $HgCl_2$ ½ oz., HCl 1 fluid oz., aniline blue 5 grs. (a colouring for safety), water 3 gallons (1 in 962).

Krönig and Paul in 1897 showed that mercury salts followed a general rule that the germicidal power depends on the metallic ion, and is in proportion to the degree of ionisation, so that a 1 in 500 solution of $HgCl_2$ is much less than twice as active as 1 in 1000: moreover, the chloride is more active (in equivalent solutions) than the bromide, and 4 times more active than the cyanide, which is almost non-ionised. Solutions of the *oxycyanide* are used in surgery, are distinctly *alkaline*, and only slightly precipitate albumen; a strength of 1 in 1500 is antiseptic, does not readily attack instruments, and is not irritant. *Mercuric iodide*, dissolved in potassium iodide, is a powerful disinfectant, and is made

up as 'iodic hydrarg.' It is less affected by albuminoids and less irritant than the chloride, and is incorporated in a disinfectant soap. *Mercury-zinc cyanide*, 'Lister's antiseptic,' has the disadvantage of being of variable composition. A great number of organic mercurial compounds, introduced into medicine and surgery, trace their main effect to an antiseptic or germicidal action. 'Sublamin,' mercurie-ethylenediamine sulphate (43 p.c. Hg), is easily soluble in water, is much less irritant than mercuric chloride, does not coagulate albuminous solutions nor precipitate soap, and is a valuable hand-disinfectant.[1] 'Protectyl' contains about 96 p.c. water, 1 p.c. salicylic acid, 0·2 p.c. mercury, and about 3 p.c. gelatin.

Silver nitrate stands next to mercuric chloride in germicidal power, and has similar limitations in its use, with the additional one of being precipitated by chlorides. The writer found that 1 in 1000 killed *B. coli* and *S. py. aureus* in 24 hours, but a small quantity of chloride or organic matter prevented the effect. Among other silver salts are the citrate, '*Itrol*,' recommended as a non-irritant antiseptic dusting for wounds (Pharm. Zentr. 38, 460); 'Actol,' the lactate, for antiseptic injections; 'Tachiol' silver fluoride, easily soluble, and a powerful non-toxic bactericide specially useful for the urinary tract (1 in 1000 to 1 in 5000). Chiefly with the object of avoiding irritant action, incompatibility with chlorides, and coagulation of albuminoids, a large number of organic preparations of silver have been introduced, such as 'argentamine' (ethylenediamine-silver-phosphate), and the proteid compounds 'argonine' (casein), 'argyrol' (gluten), 'largin' (albumen), and 'protargol' (protein). A report to the British Med. Assoc. in 1906 gives the time in minutes required to kill *S. py. aureus* by the preparations used as: silver nitrate ($\frac{1}{2}$ to 2 p.c.), 2 to 5; protargol (2 to 4 p.c.), 3 to 5; largin (10 p.c.), 2 to 5; argonine (5 p.c.), 3 to 6; whilst argyrol and 'collargol' (colloidal silver, J. Soc. Chem. Ind. 1903, 315) had very little bactericidal power (Lancet, 1907, i. 675). Many of these are destructive to gonococci and to ophthalmic disease organisms.

Osmic acid was found by Koch and Klein to be powerfully bactericidal: it is very poisonous and a strong oxidiser. The former stated that an extremely dilute solution of *potassium auricyanide*, 1 part $Au(CN)_3$ in 2 millions, checked the growth of *B. tuberculosis*.

Chick and Martin (J. of Hyg. 1908, 634) observe that for spores, metallic salts rank highest as germicides; with mercuric chloride, the reduction of efficiency caused by blood serum is much greater than with phenol.

Compounds related to the alcohols. It has long been known that 'wood spirit,' crude methyl alcohol, in a dilution as low as about 5 p.c., can kill insects and most micro-organisms, and preserve perishable organic materials owing to the tar products that it naturally contains. The alcohols, by themselves, are only efficient in a very much higher strength by coagulating albumen and (when absolute) by withdrawing water. Wirgin (Zeitsch. Hyg. 1904, 46, 149) has tested methyl, ethyl, butyl, and amyl alcohols with anthrax spores, and *S. py. aureus*, and concludes that the disinfecting power is low, that it increases with the molecular weight, and that there is scarcely any action on dry spores. It has been suggested to add alcohol vapour in steam disinfection, but Seige (Chem. Zentr. 1902, 1, 130) finds no advantage. Hand-disinfection with alcohol is not reliable (Goenner; Harrington, Boston M. J. May 21, 1903), although Hansen found that epidermal bacteria, especially in suppurating eczema, are, when moist, destroyed in one minute by absolute, and in most cases by 50–60 p.c. alcohol (Centr. Bakt. 1907, 466). *Glycerol* in strong solutions (25 p.c. and upwards), is antiseptic, but in weaker ones it rather promotes the growth of bacteria. *Allyl isothiocyanate*, mustard oil, has figured in a number of patents, and is capable of killing many organisms, but not economically.

Formaldehyde is found in commerce as the 40 p.c. solution 'formalin' or 'formol'; it is antiseptic and germicidal, and is official in the German, Austrian, Belgian, United States, and Japanese pharmacopœias. Formalin, diluted 10 times, is used for embalming and for preserving bodies for dissection and museum specimens, but for antisepsis generally, a much weaker solution is efficient. The Board of Agriculture state in their Journal of Dec. 1906, that from 2 years' experiments at Kew, they have found that fruit of all kinds immersed for 10 minutes in a solution of 3 pints formalin to 10 gallons water (=$1\frac{1}{2}$ p.c. CH_2O), then allowed to drain and dry, keeps 10 to 21 days longer than when untreated; and that one lot of liquid can be used for a number of batches. The writer and Dr. Foulerton have proved that 1 in 50,000 of formaldehyde (=1 in 20,000 of formalin) suffices to keep milk sweet for 24 hours, even in warm weather, without injury to health (Pub. Health, May, 1899; Lancet, 1899, 1427, 1571). Apparently because experiments with larger doses showed effects on nutrition, the British Dept. Committee on Preservatives, in 1901, recommended 'that the use of formaldehyde or formalin or preparations thereof in foods or drinks be absolutely prohibited.' And yet its agency in the preservation of food is as ancient as that of salt. The disinfectant and preservative power of wood-smoke is in part due to formaldehyde, which is present on the surface of smoked provisions,[1] and was found by Trillat in amounts varying from $\frac{1}{10000}$ to $\frac{1}{100000}$ of the weight of the substance consumed, in the smoke of carbonaceous combustibles, especially wood and cellulose. In tobacco smoke, he found 0·05 to 0·12 p.c., and in soot from house chimneys, 0·28 to 0·35 p.c. as paraformaldehyde. Typhoid and cholera organisms were killed by products from the combustion of 2 grams of sugar passed into a 12 litre vessel, and by burning 4 kilos. of sugar in a room of 100 cub. metres 'even very resistant organisms were destroyed.' (Rouguier has made this the basis of Fr. Pat. 360476, 1905.) With straw, the best results were obtained by burning it in a heap of alternate dry and wet layers: using 18 kilos. of

[1] Schrauth assigns a high disinfecting value to the sodium salt of hydroxymercury-benzoic acid (J. Soc. Chem. Ind. 1910, 1328; 1911, 382).

[1] Perrier finds $\frac{1}{10000}$ to $\frac{1}{1000000}$ in bacon, ham, sausages, and herrings; remarks that a strict regulation against formaldehyde would forbid these foods; and contends that a limit should be fixed instead of prohibition.

straw in a room of 140 cub. metres (4944 cub. feet), *B. coli* and *diphtheriæ* were destroyed after contact with the smoke for 12 hours; the room temperature rose to 35°, and up to 2 grams of formaldehyde were generated per kilo. of straw (Compt. rend. 138, 1613; 139, 742; 140, 797; 141, 215; 150, 339). This explains some old methods of disinfection, which Trillat still recommends for emergencies, but admits they are inferior to the use of pure formaldehyde in solution or vapour.

H. Will (Zeitsch. Brauw. 1905, 28, 330, 347) gives formalin a very high place among brewery disinfectants. He notices, like other observers (Kinzel; Slater and Rideal, Lancet, April 21, 1894), that it is more powerful against bacteria than against yeasts and mould fungi. Limits recorded as preventing development are: sarcinæ and bacteria, 0·003 to 0·031 p.c.; yeasts, 0·007 to 0·062 p.c.; moulds, 0·031 to 0·125 p.c.

Advantages in formaldehyde disinfection are: (1) that it can be easily applied in the state of gas or vapour for fumigation; in the liquid condition as spray, wash, dipping, or in higher dilutions as an antiseptic, or in the solid form as its polymers, compounds, or mixtures; (2) that unlike mercuric chloride and many other agents, it is not thrown out of action by albuminous matter or by most chemicals; (3) that it is effective in strengths which are not irritant or poisonous, and do not injure fabrics or metals. At quarantine stations, large quantities of bulbs, roots, nuts, fruits, &c., coming from plague or cholera-infected regions are disinfected by immersion in a 5 p.c. solution of formalin, which does not injure the food value and much retards decay. In the Linley process, meat is treated with formaldehyde vapour, '1 oz. formalin per cub. foot of space in the chamber,' the gas after a time removed by a fan, and the meat frozen for shipment. A report to the Local Government Board, in 1909, by Buchanan and Schryver, on Formaldehyde Preservation of Meats (Food Report, No. 9), states that the gas commonly penetrates for about 20 mm. under a thin layer of connective tissue, that the amount absorbed often reaches 1 in 3500, that it is reduced or removed by boiling or roasting, but that grilling seems to make it penetrate further.

In surgery, formaldehyde and its preparations have been of wide service. Salter (Guy's Hosp. Gaz. Oct. 1896) states that it rapidly kills the fungus of ringworm. As pigment and spray (1 or 2 p.c. formalin), it has been successful in diphtheria: in such strength, it quickly kills other non-sporing organisms, including, according to E. Blake, the 'staphylococcus of eczema.' In most cases, ½ p.c. solution is sufficient. 'Lysoform' is a liquid potash soap containing formaldehyde, suitable for operations and for instrument and hand disinfection. The alkali promotes the effect and penetration; Geronzi found that the addition of 5 p.c. of sodium carbonate to the 5 p.c. formalin which he successfully used for obstinate ear disease increased the tolerance and enhanced the germicidal power (Arch. Ital. di Otologia, 1903).

Formaldehyde antiseptic powders for dressing are: 'Amyloform' (starch); 'Proteol' (casein); 'Steriform' and 'Sterisol' (lactose); 'Glutol' (gelatin). These, especially the last, when moistened as in a wound, slowly regenerate formaldehyde. Formalised gelatine is now largely used with success instead of surgical collodions. *Formamint tablets*, 'for infectious diseases and as a prophylactic,' are said to contain 0·01 gram of $C_{11}H_{12}O$ in each, combined with milk sugar (Eng. Pat. 2672, 1906; Pharm. J. 1907, ii. 838). M. Jones states that with *B. diphtheriæ* the R. W. coefficient is only 0·01 as against 0·30 for cyllin pastiles.

Paraform, paraformaldehyde, trioxymethylene, or 'triformal,' is a solid polymer, only slightly soluble in cold water, and dissociated into CH_2O gas on heating. It was introduced as an internal antiseptic and for disinfecting instruments, and said to be as active as β-naphthol, but its chief use is for evolving formaldehyde either alone or in mixture, for which a large number of methods have been proposed, many of them patented. Mixtures with Na, Ba, or Sr peroxide, when brought into contact with water, yield formaldehyde and hydrogen peroxide: it is stated that 'Autan' contains 1 part of paraform to 2 of BaO_2 (Lancet, 1908, i. 139), and that 50 grams mixed with water kills all organisms in a cubic metre of air bubbled through it (Fr. Pat. 366605, 1906).

Room disinfection with formaldehyde cannot be economically effected by simply evaporating the solution; under ordinary circumstances, only a portion of the substance is volatilised, the remainder polymerising and remaining behind as a solid, while reliable disinfection requires a definite large volume of gas to be produced in a short time. For this object, very numerous methods and apparatus have been devised, which may be grouped as follows:—

A. Direct production of CH_2O gas, by passing methyl alcohol vapour and air over hot surfaces of platinum (Hofmann) or partly oxidised copper (Loew). The various lamps on this principle have had the faults, among others, that the oxidation is incomplete and inconstant. Kenwood, however, found in trials with a lamp using platinised asbestos, that sufficient formaldehyde can be generated from 1½ litres of methyl alcohol to disinfect a room of 2000 cub. feet.

B. Heating the solution (formalin) under pressure. Trillat observed that this almost entirely prevented polymerisation, especially if a neutral mineral salt, such as calcium chloride, was added to raise the boiling-point. In his *autoclave*, he uses 'formochloral' (formalin with 10 p.c. of $CaCl_2$) in the proportion of about 1 lb. to 1500 cub. feet. When the pressure has reached 35–40 lbs. (135°–140°), the gas is injected into the closed room through a copper jet passing through the key-hole, at such a rate that the pressure is maintained. By this method, Kenwood obtained sterilisation of diphtheria swabs, and the writer with various articles infected with *B. typhosus*, *diphtheriæ*, *coli*, *S. pyogenes aureus*, and anthrax spores, found that in 24 hours all were sterilised, whilst fabrics, furniture, metals, and leather were not injured. With the Thursfield disinfector, evolving steam and formaldehyde vapour, the writer found that, per cubic metre of room space, 7½ c.c. of formalin vapourised with not less than 30 c.c. of water was sufficient for killing anthrax spores in 6 hours, but the disinfectant had little penetrating

power, especially through wet material (J. R. San. Inst. 1903, 508).

C. Formalin, mixed with glycerol, is distilled at nearly the ordinary pressure, as in the Trenner-Lee, Lentz, and Lingner apparatus. The latter, according to the Russian National Health Society's Journ. 1900, was mainly instrumental in extinguishing the plague at Astrachan, in 1899. Klein (report of 1902), by 3 hours' exposure in a sealed room with the Lingner generator, sterilised anthrax spores and tubercular sputum. Houston and Newman also report favourably (Practitioner, Sept. 1902).

An important point to notice is that in method (B), the CH_2O is chiefly liberated at the beginning of the operation, in (C) at the end, mixed in the latter case with steam and glycerol spray, which deposits as a film on the surfaces, and assists in the penetration and disinfectant action.

D. Formaldehyde and acetone are used in a complicated process of Fournier's, in which ammonia is also introduced (Eng. Pat. 10348 of 1908: he has a number of other allied patents).

E. Combined disinfection with SO_2 and formaldehyde has often been proposed, since both have a reducing action and therefore should not interfere with one another. Guasco and Jerome assert that it is more effectual than either substance alone, and their French patent, 379098 of 1906, claims admixture with 'sulphurous gases' as preventing polymerisation.

F. Evolution by mixing with other chemicals. Dehydrating agents disengage very little CH_2O gas from formalin, since most of it polymerises. With quicklime, the writer has only obtained 8 p.c. of the theoretical yield (*cf.* Eng. Pat. 8259, 1899; Fr. Pat. 323041, 1902; and U.S. Pat. 790468, 1905). Carteret observes (Compt. rend. 1908, 146, 819) that 1 part formaldehyde and 2 parts bleaching powder added to 3 parts water evolve 70 p.c. of the theoretical yield of CH_2O and no Cl, while the heat gradually rises to 108° (D. R. P. 217944 of 1908). Potassium permanganate behaves similarly, generating great heat, with a variable loss of substance by oxidation: U.S. Pat. 885223 relates to a mixture of this kind. The action of peroxides has been already mentioned.

G. The simplest process is heating paraform by a small flame (avoiding ignition), when it melts and is resolved into CH_2O. The 'Alformant,' or Schering lamp, uses 1-gram tablets placed in a perforated cup, and it is directed to use 10 tablets per 1000 cub. feet with 6 hours' exposure. The writer found that this quantity killed *B. coli*, *typhosus*, *diphtheriæ*, and *S. py. aureus* in 20–24 hours, and that double the quantity in the same time killed *moist*, but not always *dry* anthrax spores. He recommended spraying with ½ p.c. solution of formalin before using the lamp, as the gas is evolved with insufficient moisture. The latter defect is remedied in the 'hydroformant' lamp, in which 12 ozs. of water in an annular vessel is simultaneously evaporated. Rosenau considers this method of generating CH_2O useful for the disinfection of closets and small enclosures of less than 100 cub. feet, with not less than 12 and preferably 24 hours' exposure, and not less than 2 ozs. of paraform per 1000 c. feet (about 2 grams per cub. metre). Klein, Houston, and Gordon's report to the London County Council, in 1902, records that with 23 grams of paraform per 1000 c. feet, *B. typhosus*, *diphtheriæ*, *pyocyaneus*, and *S. py. aureus* were killed in 5 hours, but not anthrax spores nor (with certainty) *tuberculosis* in sputum. It will be noticed that the time is not even that given in the directions issued with the lamp, and the humidity and temperature of the room are not stated. Allan, Newman, and Cribb had previously obtained generally satisfactory results with 10 grams paraform per 1000 cub. feet, under moist conditions (Brit. Med. J. Aug. 13, 1898). Kenwood's experiments pointed to an average of 25 grams per 1000 cub. feet being necessary. Werner and Bonhoff (Berl. Klin. Woch. 1904) find that tubercular sputum is certainly disinfected by 5 grams per cub. metre (141 grams per 1000 cub. feet) acting for 7 hours, which is double the quantity Flugge first recommended. In Breslau a large number of formaldehyde disinfections are carried out for scarlet fever and measles, and the disease has in no case recurred in the same room.

Method (G), as the writer stated in 1897, should always be a double one: (1) spraying lightly and evenly with a ½ p.c. solution of formaldehyde (2 ozs. formalin per gallon), this strength being sufficient, and not needing special precautions of masking or gloves; (2) fumigating with 10 to 20 grams paraform per 1000 cub. feet and 24 hours' contact. With larger rooms than usual, it is better to use two or more lamps than to put an extra number of tablets into one lamp.

Spraying with the solution should, in fact, be the invariable practice except with the large CH_2O generators, which are capable of filling the room also with steam and spray. When spraying is used alone, there is a danger of not penetrating into crevices, and the solution must be of higher strength; Dr. Mackenzie's extensive experience in the disinfection of houses and hospital wards, proved that 1 p.c. CH_2O (4 ozs. formalin per gallon) is attended with success: he adds 5 ozs. glycerol per gallon of formalin to prevent too-rapid drying. Thresh and Sowden in 3 to 4 hours sterilised *diphtheria*, *typhosus*, *cholera*, *pyog. aureus*, and *prodigiosus* with ½ p.c. CH_2O, but *pyocyaneus* (on whitewash) only with 2 p.c.; they, therefore, recommend the latter strength.

Where the space has to be occupied soon afterwards, any residual formaldehyde can be neutralised by volatilising ammonia, which forms the inodorous solid hexamethylenetetramine $C_6H_{12}N_4$. This substance retains some antibacterial properties: under the name of *Urotropine*, it is a serviceable antiseptic in cystic affections, and is administered to typhoid convalescents to destroy the bacilli of the disease, which, for a long period, continue to be discharged in the urine. As an alternative, since the drug may act unfavourably on the patient, or as an additional precaution, the urine can be sterilised externally with 1 in 1000 of sulphuric acid. Urotropine is the basis of a large number of antiseptic preparations, such as 'Helmitol' (Chem. Zeit. 1901, 25, 1045; Z. Klin. Med. 38, 4, 5, 6).

Disinfection of excreta is attained by mixing

with 3 to 5 p.c. of formalin and keeping in a closed vessel for at least an hour. Rosenau states that fæces are rendered sterile at the end of 10 minutes by an equal volume of a 4 p.c. solution of formalin. Houston prescribes 1 to 2 pints (according to bulk) of 5 p.c. formalin, acting for at least an hour (Practitioner, Sept. 1902).

Formaldehyde, as an insecticide, is much inferior to SO_2, although Brough (J. Mass. B. of H. March, 1898, 51) observed, in his disinfections with the former gas, that all the flies were invariably killed, and generally the bed-bugs. It is an excellent deodorant.

No acidity is produced by continuous spraying or distillation of formaldehyde, therefore it is not readily converted into formic acid in this way.

Formic acid.—We have discussed the germicidal action of acids generally in an earlier section of this article. Formic acid has this power to a considerable extent, and is a strong antiseptic. Kitasato's results, as summarised by Horrocks, gave acetic acid a slightly higher activity in nutrient media, stating that with *B. typhosus* the amounts p.c. in cases of (1) growth, (2) growth restrained, (3) no growth, were respectively: formic acid, 0·22, 0·278, and 0·356; acetic acid, 0·2, 0·225, and 0·3; with *Sp. choleræ*, formic, 0·11, 0·167, 0·22; acetic, 0·1, 0·153, 0·2. But very different results are obtained in water and most organic solutions. The writer has found that *typhosus* is killed by 0·5 p.c. of formic acid in less than 15 minutes and by 0·1 p.c. in about 30 minutes; and in 1907 he made the R.W. typhosus coefficient of formic acid many times higher than that of acetic. He also found the preservative action to be higher: with vegetable substances, 1 p.c. of formic acid was equal in effect to 5 p.c. of acetic (time of trial, 2 months). Raw fish were mounted in 0·53 p.c. formic, in 5 p.c. acetic, and in 0·3 p.c. boric, acids, heated for 20 minutes to 80°, and the jar closed with cotton wool; in a week, the last was brownish, disintegrated, and uneatable, though not distinctly putrid; while the first two kept sweet and of natural characters for 3 months. Experiments with bread-pulp infected with a mixed mould-growth proved that 0·1 p.c. of formic acid entirely inhibits the growth for several days, even under the most favourable conditions of culture. But in the destruction of the spores, formic acid is less effective than formaldehyde. Lebbin (Chem. Zeit. 1906, 30, 1009) effectively preserved different classes of foods by 0·15 p.c. of formic acid, and others have proved that in the quantities mentioned above it is physiologically harmless; the taste is more pleasant than acetic acid, and the odour is not noticeable. B. H. Smith (J. Amer. Chem. Soc. 1907, 1236) preserved vegetables with formic, with salicylic and with benzoic acid, in unprotected jars. Under conditions in which the untreated samples became sour and mouldy in 2 days, 0·1 p.c. formic acid preserved them for 7 days, 0·3 p.c. for 12 to 18 days, 0·5 p.c. for 25 days, 0·7 p.c. and 1 p.c. for 45 to over 85 days, and 2 p.c. for over 85 days. He states that 0·1 p.c. of benzoic acid kept his sample for 85 days, whilst with the same quantity of salicylic acid it was sour in 9 days. In ordinary preserving practice, as we have seen, the articles would have remained good for the longer time with the smaller quantities of formic acid, which, even if it must be applied in a somewhat higher proportion, is from physiological and physical reasons preferable to salicylic or benzoic. The chief formic acid preservatives used in commerce, mainly for fruit preparations, are 'Werderol' and 'Fructol' (10–14 p.c. formic acid, '1–1½ p.c. of the liquid to be added'); and 'Alacet' (made synthetically from CO and NaOH at the Nitritfabrik, Köpenick, about 50 to 60 p.c. formic acid, 'use 0·3 p.c. of the liquid'). The result in the three cases would be about 0·14–0·18 p.c. of the acid. In an investigation of these articles by Croner and Seligmann (Zeitsch. f. Hyg. 1907, 56, 387), they find that inhibition of moulds, yeasts, and acid-forming organisms begins at 0·15 p.c. formic acid, that sterilisation is effected in 24 hours by 0·2 p.c., and in 10 to 30 minutes by 1 p.c.

Only the free acid is active against organisms, although the salts do not favour the growths as do the alkaline acetates. Sodium formate helps the solubility of many antiseptics without lessening their power, therefore figures as an adjunct in a number of patents.

Acetic acid is one of the most anciently used of preservatives; 'aromatic vinegar,' a more or less concentrated acid containing essential oils, had a partially-justified reputation against infection. The writer finds that *B. coli* is killed by 5 p.c. HĀ in 5 minutes, by 2·5 p.c. in 15 minutes, while with 0·5 and 0·1 p.c. it is alive after 40 minutes. *Pyroligneous acid*, or crude wood vinegar, owes its antiseptic power chiefly to the presence of creosote and formaldehyde.

Acetyl peroxide and benzoyl-acetyl peroxide are stated by Freer and Novy (Amer. Chem. J. 1902, 27, [3] 161) to be strongly germicidal, since solutions corresponding to 0·037–0·074 p.c. of the former, or 0·056–0·112 p.c. of the latter, =0·005–0·01 p.c. of active oxygen, destroyed within a minute all known disease-producing bacteria, and even spores of *B. mesentericus*, which are not killed by 5 p.c. phenol; whilst H_2O_2 solution containing 0·05 p.c. of active O was without action on many bacteria even in 60 minutes. Benzoyl peroxide had no oxidising action, and was without effect on bacteria. A solution of acetyl peroxide was introduced under the name 'acetozone,' but the title is now applied to a more convenient and stable mixture of the benzoyl-acetyl compound with infusorial earth, said to be useful in typhoid, dysentery, and cholera (Lancet, 1904, ii. 1160; Brit. Med. J. 1907, i. 634).

Propionic acid has been tested comparatively by Duggan (Amer. Chem. J. 7, 62) with the highly resistant *B. subtilis*. He gives as the strengths necessary for killing: formic acid, 7 p.c.; acetic acid, 9 p.c.; propionic acid, 12 p.c. (numbers proportional to the molecular weights). According to A. C. Jordan (Practitioner, Sept. 1902, 297), 0·1 p.c. of *butyric acid* in broth tubes infected with vigorous *B. coli* or *typhosus* caused them to remain sterile; *S. pyog. aureus* required 0·2 p.c. *Valeric acid* is a feeble antiseptic, but has been introduced along with a little creosote, as an internal antiseptic called 'geosote.'

Oleic acid, the fats, 'Lanolin,' &c., have no

antiseptic power in themselves, but when applied to the skin may prevent infection by the exclusion of germs. Vicario, however, observed that the fatty matters sometimes already contain germs, and Baldas (Giorn. R. S. Ital. d' Igiene, Feb. 1901) proved that *B. coli* and *typhosus*, *S. pyog. aureus* and *albus*, retained their virulence in oils for 2 months; therefore ointment bases require to be sterilised by heating to 100°, or preferably to 120°, as various bacilli survive in oil far longer than in aqueous solution. In fatty media antiseptics and disinfectants, as a rule, are much less active than in water, hence the ineffectiveness of carbolised oil as shown by Koch and Breslauer. Lanoline and cold cream contain water, so can enable agents in aqueous solution to come in contact with micro-organisms. Some metallic oleates are parasiticide: cupric oleate in ringworm and favus (Lancet, 1907, i. 510); mercuric oleate for pediculi; zinc oleate is said to cure chronic eczema.

Vegetable acids like tartaric, citric, and malic have the general power of inhibiting bacteria which prefer a neutral to an acid medium, but their effect is much less than that of mineral acids, and, as is well known, their solutions quickly become mouldy in warm weather. Citric acid was formerly recommended for sterilising water: Dr. Christmas in 1892 stated that cholera organisms were killed by 0·08 p.c. and typhoid by 0·10 p.c. Kitasato's figures for tartaric, citric, and malic acids added to neutral media containing *typhosus* are in p.c.'s: growth, 0·338; growth restrained, 0·384; no growth, 0·476. Succinic acid is slightly antiseptic. 'Alphogen' or 'Alphozone,' succinyl peroxide, is said to be a powerful germicide (Brit. Med. J. 1905, i. 1150; Lancet, 1905, i. 367).

Benzoic acid is strongly antiseptic in solution and vapour, and to a rather less degree in its soluble salts. It dissolves in about 400 parts of cold water, and the saturated solution kills *B. typhosus* in a few minutes. When molecular proportions, *i.e.* sodium benzoate 0·026 p.c., potassium benzoate 0·029 p.c., benzoic acid 0·022 p.c., are separately mixed with milk, the writer observes that all retard the souring, the acid more than its salts, but the effect comes to an end sooner than with inorganic salts like the fluorides, since benzoic acid is itself decomposed by some organisms. Not being poisonous, it has been much used as a food preservative, particularly in countries where salicylic acid was forbidden. Following a report of the Referee Board of the U.S. Board of Agric. that doses of benzoates under 0·5 gram per day were not injurious to health, and that even 4 grams per day did not act as a poison, the U.S. Board, in Pamphlet 104, 1909, have announced that they will make no objection to the use of sodium benzoate in food, provided it is plainly labelled on each package, both as to presence and quantity. The taste and odour are difficult to mask. It has long been used as an antiseptic in surgery, *e.g.* in 'Friar's Balsam' (tinct. benzoini co). *Benzoic aldehyde* is official in the U.S. Pharmacopœia, and in the form of commercial oil of bitter almonds owes its parasiticide power in ointments mainly to the hydrocyanic acid it contains, which, of course, necessitates care in use. *Benzoyl-sulphonic-imide*, Saccharin' or 'Gluside,' has some preservative power, and has been given internally to stop decomposition of urine in cystitis, but its use for sweetening is less on account of this power than because it is itself unfermentable.

Salicylic acid.—The saturated aqueous solution contains 1 in 500: tested with *typhosus*, *pyog.*, *aureus*, and *anthrax*, Westcott found that in 3 hours only the former was killed. As a food preservative, it is about equal to benzoic, their relative activities varying under different circumstances. Its physiological effect is more distinct than that of boric or formic acid or formaldehyde in the small quantities required, but there is no clear evidence that it causes injury to adults if the amount is limited. The British Depart. Committee's suggested restriction is that it 'be not used in a greater proportion than 1 grain per pint in liquid food and 1 grain per lb. in solid food,' or 0·0114 and 0·014 p.c. respectively, which practically would amount to a prohibition, since moulds and ferments are only reliably inhibited by 0·1 p.c., the amount commonly employed, though often exceeded. Addition of the acid to foods is forbidden in France, Austria, and some other countries. Traces are present in a large number of fruits (Analyst, 1903, 149). 'Salol' is phenyl salicylate, an internal antiseptic which is decomposed in the duodenum into phenol and salicylic acid. According to Lowenthal, when mixed with pancreatic juice, it rapidly kills *Sp. choleræ* (Compt. rend. 107, 1169). 'Salophen,' *p*-aminophenyl acetyl salicylate, is said to have a rather stronger antiseptic power (Practitioner, March, 1907). A large number of derivatives of salicylic acid have been introduced, and many of them patented.

Cinnamic acid, at 2 p.c., prevents the growth of bacteria, and at 4 p.c. destroys them. It is contained in Peru and storax balsams, which are parasiticide in skin diseases. Fr. Pat. 371091 preserves butter by enclosing it in a wrapper impregnated with cinnamic acid, which 'prevents butyric fermentation.' *Acetyl-o-coumaric acid*, Tylmarin,' is another internal antiseptic, said to have a R.W. coefficient of 4·5.

Tannin is antiseptic to proteids through its property of forming with them insoluble compounds such as leather, but none of the tannin extracts have even the power to preserve their own solutions.

Hydrocarbons, essential oils, and camphors.—Petroleum, mainly consisting of hydrocarbons of the paraffin series, has long been a well-known insecticide, and is mentioned by Marco Polo in the 13th century as used to kill acari in mange. It has been stated that articles are disinfected by dry-cleaning with petroleum-benzine, or by benzene. Farrel and Howles (J. Soc. Dyers, 1908, 24, 109, 166), however, find that acting on infected threads for 6½ hours, neither benzene (C_6H_6) nor petroleum-benzine killed *typhosus*, whereas carbon tetrachloride killed it in 30 minutes, whilst 'benzine soap,' dissolved in benzine, has no germicidal power.

Perfumes, chiefly composed of terpenes and their oxidised products (*e.g.* the camphors, menthol, thymol, and eucalyptol), have a limited sanitary value. All of them are very sparingly soluble in water, but impart to it a more or less

antiseptic effect. Early estimates of their power have not been concordant, chiefly owing to their having been tried variously in aqueous or alcoholic solution, or in suspension. A saturated solution of *thymol* in water (0·3 p.c.) arrests fermentation and putrefaction. Peppermint (containing *menthol* and menthane) has had a high reputation, and a number of recipes for 'plague water, have it as a basis. The use of hops in brewing partly rests on the power of the essential oil to check fermentation. 'Terebene,' made by the action of H_2SO_4 on terpentine, was once reputed as a disinfectant, but now hardly figures except as terebene soap. Among other artificial products from turpentine are *terpin hydrate* (said by Colpi to arrest the growth of tubercle bacilli in 0·25 p.c. strength), and *terpineol* (anthrax is stated to be killed by 1 p.c., and staphylococci by 10 p.c. in 60 minutes: (H. Marx, *v. infra*; *also* D. R. P. 207576, 1906)).

Camphor is much spoken of as a personal prophylactic, but there cannot be sufficient of the vapour to sterilise the air. It is an ingredient in many remedies for cholera and diarrhœa, and in several 'block disinfectants' such as 'Sanoscent,' 'Camphortar,' &c. *Eucalyptus globulus* and other species which have long been famous as antimalarial, are largely planted on the Continent in marshy districts. The essential oil is decidedly germicidal, and has been given with some success in typhoid, and also against tape- and threadworm.

Pinol is a liquid of similar character from *Pinus pumilo*. H. Marx has investigated the action of various perfumes on anthrax and *S. pyog. aureus* (Centr. Bakt. 1903, [1] 33, 74). Kobert (Chem. Zentr. 1907, i. 419) finds that the terpènes have, by themselves, in general only a weak antiseptic action. The proportions needed for sterilising exceed the solubility in water, and can only be reached by a spirituous solution or an emulsion.

But it has been recognised, since Schönbein pointed out the fact about 1840, that essential oils have a disinfectant power conferred on them by their slow oxidation in the presence of air and moisture, whereby ozone is produced; that as long as air and oil are present, the ozone is continually regenerated and absorbed, forming oxidising and antiseptic products, which dissolve in the water, along with peroxide of hydrogen. This was the principle of the 'Sanitas' patent 274, 1876.

Aromatic nitro- compounds, such as nitrobenzene, have often been proposed as disinfectants, but are precluded by their odours, poisonous action, and sparing solubility. Trinitrophenol, 'picric acid,' is rapidly fatal in saturated solution (about 1 p.c.) to bacteria and spores, but causes yellow stains, is irritant and very poisonous. Cotton wool, soaked in the solution, is used very successfully in the aseptic treatment of burns; hence it is recommended by H.M. Inspector of Explosives to keep handy for this purpose. Potassium dinitro-ortho-cresol, 'Antinonnin,' 1 in 400, is destructive to all common injurious parasites, and does not injure plants.

Aniline is open to the same objection as nitrobenzene. A number of aniline dyes are germicidal, owing to their power of penetrating and combining with living tissue. This action is very variable, but it is stated that 1 p.c. prevents development of organisms, whilst 1 in 500 to 4000 retards their growth. Methyl violet or 'pyoktanin,' gentian violet, certain auramines, safranine, methylene and toluidine blue have been used in surgery and in malaria. Malachite green, injected into the blood, kills *trypanosoma* in 48 hours (Brit. Med. J. 1904, ii. 1449, 1645; Deutsche Med. Woch. Leipzig, 1906, 21, 463). Methylene blue, with atropine and benzoic acid, according to Lelean (Lancet, May 3, 1902), was the only drug he found of use against *Bilharzia*.

Naphthalene, Quinoline, Pyridine, and related bodies.—Naphthalene is feebly antiseptic, but not a disinfectant. It is useful by its odour to drive away domestic insects.

Beta-naphthol is official in the British (1898) and in a number of other Pharmacopœias, the dose in the former being 3 to 10 grains in a cachet for internal antisepsis, especially in typhoid and in cholera as a preventative. Its solubility in water is increased by boric acid. Schneider observes that naphthols dissolved in alkaline carbonates have greater disinfectant power than alkaline naphtholates; the former solutions contain naphthol in the free state. He states that staphylococci and typhoid are killed in a short time by 0·5 to 1·0 p.c. of β-naphthol alkaline carbonate solution (Zeitsch. Hyg. 1906, 52, 534).

Ointments containing 10 to 15 p.c. are efficient in scabies and psoriasis. 'Betol,' β-naphthol salicylate, is less soluble than naphthol, and is now seldom used. 'Alphol' is its analogue from α-naphthol, and is very similar. A number of easily soluble compounds have been introduced, such as the β-naphthol sulphonates, 'Asaprol' or 'Abrastol' (calcium), and 'Alumnol' (aluminium). Helbing states that an aqueous solution of the latter, 1 in 250, prevents all growth of gonococci, pus cocci, and allied bacteria. Bechold (Zeitsch. angew. Chem. 1909, xxii. 2033) finds the odourless and non-poisonous halogen-*substituted* naphthols more powerful than any disinfectant except $HgCl_2$, and that tribromonaphthol kills staphylococci in dilutions of 1 in 250,000.

Pyridine is volatile, mixes freely with water, and is strongly insecticide, but has a very unpleasant odour, which has militated against its use in horticulture. Tobacco smoke, indeed, owes its powers, not to nicotine, which is almost entirely decomposed by the heat, but to the products pyridine and its homologues, which are formed. Tessinari destroyed the bacilli of cholera and pneumonia by tobacco smoke passed for 10 to 30 minutes through a tube containing infected nutrient gelatin. Wynter Blyth killed the bacillus of nasal catarrh by 1 p.c. solution of pyridine and its homologues (from bone oil), or by tobacco smoke. There is proof that smokers and workers in tobacco enjoy comparative immunity from epidemics, but pyridine inhalations (*e.g.* in asthma and whooping cough) require care, as it is a cardiac depressant. The above experiments confirm the general view that disinfectant preparations containing the basic constituents of coal tar are to be preferred to those which only include the phenols.

Tobacco juice, of course, contains nicotine, and in France is sold as an insecticide under an

official guarantee as to its nicotine strength. In England, a solution of the pure base in water is sometimes used as more definite. Richard's cakes for fumigation are nicotine and camphor: the writer found a sample in 1909 to contain 1·17 p.c. of nicotine and to be completely volatile at a gentle heat.

Chinosol is potassium-oxyquinoline-sulphonate, $C_9H_6NO{\cdot}OSO_3K$, a yellow powder easily soluble in water to an acid yellow solution, which does not stain, has only a slight aromatic odour, is permanent on keeping, is not poisonous, and does not coagulate albumen. It has been patented as a disinfectant, and more especially as an antiseptic. Klein compared its action on *S. pyog. aureus*, *B. coli* and *anthracis* with that of carbolic acid, and reports that a solution of the latter of 1 in 20 strength is required to kill *aureus* or *coli* in 5 minutes with certainty, whereas chinosol does this in a strength of 1 in 150. Anthrax spores are not appreciably affected in 48 hours by 5 to 6 p.c. carbolic, whereas chinosol of 1 p.c. acts germicidally on them in 5 minutes. In the writer's laboratory, *B. coli* was not sensibly affected after 4 hours by 1 in 1000 chinosol, whilst 1 in 2000 of $HgCl_2$ produced sterility under the same conditions in 15 minutes, so that it is difficult to explain the much higher powers that some observers have found for chinosol. Thresh and Sowden state that chinosol spray of not less than 1 p.c., is a reliable disinfectant (J. San. Inst. Jan. 1903). Houston did not succeed in killing *B. coli* in excreta by 1 in 75, and on linen by 1 in 62 (Practitioner, 1902, 331). On account of its acidity, it acts on iron and steel. Alkaline solutions interfere with its power: the writer showed that a soap containing 5 p.c. of chinosol was inferior to a 0·5 mercuric iodide soap. F. G. Müller reports encouraging results with chinosol in leprosy (Zeitsch. Oest. Apoth. Ver. xxxv. 858). 'Cresochin' (Pharm. Centralhalle, xxxvii. 247) is said to be a neutral sulphonate of quinoline and tricresol, which is recommended for disinfecting instruments, as it does not darken the steel.

Quinine, which has a quinoline nucleus, probably owes its action against fevers as much to its antiseptic power as to its effect on the nervous system.

A. Raal (Pharm. Zeit. 1900, xlv. 569) asserts that strongly fluorescent bodies much increase the action of sunlight on organisms, whilst they are almost inert in the dark. A 1 in 20,000 solution of acridine killed infusoria exposed to sunshine in 6 minutes; in the dark they survived for 24 hours. Similar results were noted with quinine sulphate and with eosin. The inference is that the effect is caused by the fluorescent rays. Fluoresceïn has been patented as an antiseptic by Turpin, chiefly for toilet preparations (Fr. Pat. 346363, 1904). The bromofluoresceïns, particularly eosin, are found to have greater power. He claims a large number of other phthalein compounds as disinfectants.

Certain faults of many antiseptics and disinfectants in the free state have led to an immense number of attempts to improve them by converting them into various derivatives. Although the effort to produce new proprietary substances, has given rise to a multitude of often misleading titles, many of these preparations have been proved to have utility. The modifications may be generally classified as follows:—

1. *Metallic salts.*—Compounds with the alkalis or earths are generally less active than the free substance. Other metals have been introduced, with the object of adding their special properties, as Al for astringency, Zn, Cu, Ag, and Hg for developing germicidal effect; but it must be remembered that a combination of this kind, though it may have some lateral advantages, is commonly weaker than either agent singly. The same remark applies to the two next groups.

2. *Substituted compounds.*—Those with iodine are exceedingly numerous, including a large number which have been improvements on iodoform when it was unduly valued. Where organic radicles (basic like methyl or ethyl, acid like acetyl or benzoyl) are introduced, the physiological properties are usually entirely altered.

3. *Esters*, sulphonic, and other colligated compounds which, while less poisonous or irritant than the parent bodies, slowly yield the latter by gradual decomposition. Several of these have proved of great value.

Resorcinol, *m*-dihydroxybenzene, is a powerful medicinal antiseptic, and a 1 p.c. solution kills most organisms. 'Andeer's lotion' contains 40 grains in 1 oz. water. 'Anusol' is a bismuth iodo-resorcin sulphonate. *Quinol* or hydroquinone, *p*-dihydroxybenzene, is said to be a stronger antiseptic than the last, and has been suggested for typhoid in doses of 3 to 8 grains. The ortho- compound, *catechol* or pyrocatechin, is also antiseptic. Duggan finds (Amer. Chem. J. 7, 62) that the amounts of the three isomerides required for preventing development of *B. subtilis* in broth are: ortho- 20, meta- 25, para- 30; phenol being 20 and pyrogallol 15.

Guaiacol (methyl-catechol) and *creosol* (methyl-guaiacol) are the active ingredients in wood creosotes, and have been widely useful as antiseptics and parasiticides, especially in tuberculosis. Guaiacol has an antiseptic power (but not bactericidal—see Table) 2½ times that of phenol, and a ½ to 1 p.c. solution destroys *B. tuberculosis* in 2 hours (Marfori, Ann. di Chim. 12, 3). A one in 150 solution of (Morson's) creosote kills *pyog. aureus* and *typhosus* in 3 hours (Westcott). 'Little's Soluble Phenyle' contains wood creosote, and Corfield's experiments gave it a high value for wounds and against vermin. Kenwood and Hewlett (J. R. San. Inst. 1906, 13) make its R.W. coefficient 1·2.

Pyrogallol, tri-hydroxybenzene, is antiseptic, and a 3 p.c. solution kills most bacteria, particularly aërobes, but it stains, is unstable, and very poisonous.

For general purposes of disinfection, 'coal-tar' fluids, having as their chief active constituents bodies allied to phenols, are most extensively employed. They are usually dark syrupy liquids smelling of coal tar, and may be roughly divided into two classes: (1) those which on the addition of water form a more or less clear dilution; and (2) preparations miscible with water but producing an emulsion. The former usually consist of saponified tar-acids: the *liquor cresoli saponatus*, Ph. G., consisting of

equal parts of potash soap and crude cresol heated together, is of this nature. In the manufacture of these fluids, potash soap, glycerol, alcohol, and other agents are employed to aid the solubility in water. With the second group, the mostly insoluble, active ingredients are emulsified by the aid of soda, soaps, resin, neutral oils, or gelatin.

As already indicated, the proprietary articles of this nature bearing fancy names are very numerous. Since the Privy Council Orders of 1900 and 1902, the uncontrolled sale of liquids containing upwards of 3 p.c. carbolic acid or its homologues is prohibited, and the germicidal value of the more insoluble and higher boiling-point tar acids has been recognised. The generality of commercial disinfectant fluids are now practically free from carbolic acid, and, in comparison with the latter, are non-poisonous. These disinfectant preparations should not be employed to destroy resistant spores without prolonged exposure; according to the nature and amounts of active ingredients present, they are usually germicidal with non-sporulating organisms in dilutions far greater than is the case with absolute phenol. However, the strength of these proprietary articles varies considerably, and beyond the requirements of germicidal value specified in contracts with various authorities, there is at present, unfortunately, no legal control over the efficiency of disinfectants as sold to the public. There are instances of so-called disinfectants which enjoyed great popularity and even were advocated by the medical profession, yet possessed little or no germ-killing power under the conditions in which they would be employed.

Since the adoption of the R.W. test, there has been a steady rise in the efficiency of commercial disinfectants.

Testing of disinfectants.—Before 1881, when Koch introduced the use of pure cultures, tests depending upon the prevention of putrefactive changes in various organic infusions were mainly employed, and to a great extent the antiseptic or preservative value was noted rather than the actual germ-killing power (*see* first edition of this dictionary). Since then, an increasingly large number of investigators have worked upon practical methods of testing. With the phenolic disinfectants, valuations were made upon the total amount of tar acids present, but the widely differing activity of these bodies, which is also modified according to their physical condition on dilution (in *solution*, tricresol has only one-third the germicidal value of that in *emulsion*), has led to the general adoption of bacteriological tests.

In the *thread* method (Koch), silk threads are impregnated with the test organism, and exposed for a definite time to the action of the diluted agent, and then, after the removal of adhering disinfectant, sub-cultures are inoculated from the threads to determine the survival or death of the organism (*v.* Lancet, July 30, 1900). In place of threads, small garnets can be employed (Krönig and Paul), stones of uniform size being coated from cultures of the organism, and added directly to the disinfectant, sterility being determined by inoculating sub-cultures at intervals (Zeitsch. angew. Chem. 1901, xiv., xv.). The chief points to be considered are (1) time; (2) age of culture; (3) choice of medium, reaction of same; (4) temperature of incubation and (5) of disinfection; (6) variation in vital resistance of same species and (7) of different species; (8) proportion of culture to disinfectant. In order to facilitate the comparison of disinfectants, Rideal and Walker (J. R. San. Inst. 1903, 424) suggested their carbolic acid coefficient method as the basis for a standard process. In this test, which has been extensively adopted in England and abroad, the efficiency of the disinfectant is expressed in multiples of absolute phenol performing the same work. It is briefly as follows: add 5 drops of a 24 hours' blood-heat culture of the organism in broth to 5 c.c. of a particular dilution of the disinfectant in sterile distilled water; shake and take sub-cultures with a platinum loop every 2½ minutes up to 15 minutes; incubate sub-cultures at 37° for 48 hours. Allowing 30 seconds for each operation, four different dilutions of the disinfectant with one carbolic control are tested against the same culture and under strictly comparable conditions. For example:

	Minutes	2½	5	7½	10	12½	15
Disinfectant	1 : 500	+	—	—	—	—	—
„	1 : 550	+	+	—	—	—	—
„	1 : 600	+	+	+	—	—	—
„	1 : 700	+	+	+	+	+	—
Carbolic acid	1 : 110	+	+	—	—	—	—

$$\text{Carbolic acid coefficient } \frac{550}{110} = 5$$

This test has for many years been officially used by the War Office, Admiralty, India Office and other Government departments at home and in the Colonies. It is impossible in any one test to include the greatly varying conditions of practical disinfection, but numerous modifications of the R.W. coefficient test have been suggested, mainly with the object of testing in the presence of considerable quantities of organic matter. Sterilised sea-water, urine, sewage, starch, and gelatine emulsions, nutrient broth and milk, have been incorporated with the diluting water—also testing with organisms in their natural environment, as with *coli* in sewage, in place of pure cultures. A sedimentation test for emulsified fluids allows a 1 p.c. solution to stand 24 hours before preparing final dilutions for testing (Lancet, Sept. 19, 1908). The 'Lister test' (C. J. Martin) is made in the presence of 3 p.c. of fæces, previously sterilised, dried, and powdered. Sims Woodhead and Ponder (J. Path. and Bact. 1909, 148) replace the inoculating loop by platinum spoons, used with a special sterilising apparatus, and extend the time to 30 minutes. A mean coefficient is taken for two values obtained at the beginning and end of the experiment with *B. coli* and sub-culturing into McConkey's bile-salt fluid. The Lancet (Nov. 1909) has suggested, in conjunction with the above method, a chemical analysis for the valuation of emulsified fluids as follows: 10 grams of disinfectant with 100 c.c. of water and 15 grams baryta, are heated for 30 minutes at 100° under a reflux condenser, then cooled and decanted through asbestos, washing with warm baryta water; the tar acids are extracted with ether from an aliquot portion of the filtrate, after adding calcium chloride and

acidifying with HCl, dried at 38°, weighed, and their bromine absorption determined. *Neutral* hydrocarbon oils are extracted from the baryta residue with acetone, and the insoluble soaps and resins treated with HCl and shaken out with ether. For estimation of water, 25 grams of the sample are acidified with 10 c.c. of 10 p.c. H_2SO_4 and shaken with 25 c.c. of white petroleum spirit, taking the volume less 10 c.c. of the aqueous layer after standing. In presence of the higher phenoloids, the weight of tar acids obtained is too low. The coefficients obtained for *B. coli* were found to be approximately one-third of the difference between the percentage of tar acids and the bromine value.

The germicidal power expressed in terms of carbolic acid with *B. typhosus* is shown for a number of disinfectant substances in the following table; while most of the figures are Rideal-Walker carbolic acid coefficients, some of the results have been obtained by modifications of the original test as noted, and these are obviously not comparable with the others.

Agent	Germicidal value	Observer
Absolute alcohol	less than 0·1	F. 1905
Acetic acid	0·6	R. 1907
Benzoic acid	about 5·0	R. 1910
Boric acid	less than 0·1	W. 1904
Bromine water	64	R. 1910
Cadmium chloride	1·55	R. 1911
Cadmium sulphate	1·0	R. 1911
Chinosol	0·15–0·30	Various observers
Chlorine water	28	R. 1910
Copper sulphate (calculated on $CuSO_4$)	2·0	R. 1910
Cresylic acid commercial	3·7	R. 1908
Eucalyptol	1·2	L. 1904
Formaldehyde	0·55	R. 1907
Ditto	0·75	W. 1904
Formic acid	5·7	R. 1907
Guaiacol	0·9	L. 1904
Hydrochloric acid	1·58	F. M. 1906 (with fæces and urine)
Hypochlorites (calculated on 'available chlorine')	146–220	Various observers
Ditto with 50 p.c. urine	8	K. 1906
Iodine water	100	R. 1910
Iodine trichloride	94	R. 1909
Lactic acid	1·8	R. 1910
Mercuric chloride	400–3540	Various observers
Potassium permanganate	42	do.
Pyrogallic acid	0·22	M. W. B. 1906
Resorcin	0·30	do.
Silver nitrate	15·8	R. 1910
Sodium bisulphate	4·1	R. 1908
Zinc chloride	0·15	W. 1906

M. W. B., Meredith Wynter Blyth; F. M., Firth and Macfadyen; F., Major Fowler; K., Klein; L., Lodwidge; R., Rideal; W., Walker.

The extremely high values once given for mercuric chloride were due to the powerful inhibitory action of the traces carried over with the sub-cultures in the inoculations. S. R.

DISSOCIATION *v.* CHEMICAL AFFINITY.

DISTILLATION. The object of distillation is the separation of a volatile liquid from a non-volatile substance, such as pure water from sea-water, or more commonly the separation of two or more liquids of different volatility.

The apparatus required consists essentially of four parts: a still or boiler, A (Fig. 1), in which

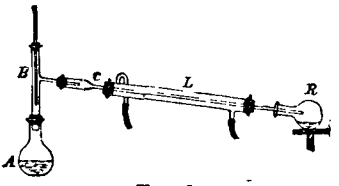


FIG. 1.

the liquid is boiled; an upright tube or head, B; a condensing tube, C, sloping downwards and cooled by suitable means—a Liebig's condenser, L, through which a current of water is passed, being generally employed in the laboratory; lastly, a receiver, R, to collect the distilled liquid. The form of apparatus shown in Fig. 2 is convenient for many purposes; the still, the head, and the condensing tube are sealed together in one piece.

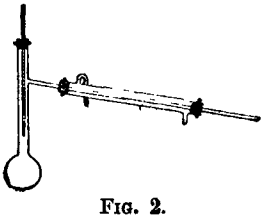


FIG. 2.

The still is usually heated by the flame of a Bunsen burner; for very volatile and inflammable liquids a water-bath is generally used, but the rate of distillation can be better regulated by a very small flame in contact with the bottom of the still; the Liebig's condenser is unnecessary for liquids which boil above 160° or 170° if the condensing tube is fairly long.

If the temperature at which the liquid boils is to be ascertained with accuracy—and this is generally the case in fractional distillation, especially in the final purification of a liquid—the following points should be attended to:—

1. The thermometer should be carefully calibrated, and it would be a great advantage if all thermometers were compared with an air thermometer, for different kinds of glass expand very differently when heated, and therefore two thermometers, constructed of different varieties of glass, will give different readings, especially at high temperatures.

2. The zero point of the thermometer should be redetermined from time to time. It is a good plan to heat the thermometer for several hours to about 300° or 360° before calibrating it; the subsequent changes of zero point, which otherwise might be considerable at high temperatures, are thereby greatly reduced (Crafts, Compt. rend. 95, 910; also several earlier papers). Thermometers treated in this manner may now be purchased.

3. All thermometers, except those which do not register temperatures higher than 60° or 70°, should contain nitrogen to prevent volatilisation of mercury in the heated stem; if the thermometer is provided with a small bulb at the top,

rise of pressure owing to compression of the gas in the thermometer is avoided.

4. The thermometer should, if possible, be so placed in the apparatus that not only the bulb but also the column of mercury in the stem is surrounded by the vapour of the boiling liquid; otherwise the following correction, which, at the best, is somewhat uncertain, must be applied :—

N = length of column of mercury in scale degrees not heated by vapour.

T = temperature of vapour (the approximate temperature directly read on the thermometer is usually sufficiently accurate).

t = mean temperature of column of mercury not heated by vapour. This temperature may be approximately ascertained by attaching a small thermometer to the other by means of thin indiarubber bands or wire, with its bulb at about the middle of the unheated column.

Correction : add $0{\cdot}000143(T-t)N$.

The coefficient 0·00016 is usually employed, but Holtzmann pointed out that this is too high, and adopted the number 0·000135. Thorpe, however (Chem. Soc. Trans. 37, 159), has shown that the coefficient 0·000143 gives the best results.[1] The table for the correction of thermometer readings is taken from Thorpe's paper, and shown in next column.

For further information *v.* article on THERMOMETERS.

5. When the amount of liquid in the bulb is very small, the vapour is liable to be superheated by the flame, and unless the bulb of the thermometer is thoroughly moistened with condensed liquid, too high a temperature will be registered. If a very little cotton wool or, for temperatures above 230°, a little fibrous asbestos be wrapped round the bulb of the thermometer, it remains thoroughly moist, and with a pure liquid the thermometer registers a perfectly constant temperature until the last trace of liquid in the bulb has disappeared (Ramsay and Young, Chem. Soc. Trans. 47, 42).

6. The barometer should always be read, and corrected to 0°, and in a long distillation or in unsettled weather it should be read frequently, for the boiling-point varies greatly with the pressure. The observed boiling-point is corrected to that under normal pressure by means of the formula $\theta = c(760-p)(273+t)$, where θ is the correction in centigrade degrees to be added to the observed boiling-point, $t°$; c is a constant; and p is the barometric pressure. For the majority of liquids the value of c may be taken, without serious error, to be 0·00012; but for water and the alcohols it is about 0·00010, and for a few liquefied gases it is considerably higher. A table of corrections was first given by Crafts (Ber. 20, 709). The values of c for a large number of substances have been collected and tabulated by Young (Chem. Soc. Trans. 81, 777; Fractional Distillation, 15).

[1] Rimbach (Ber. 22, 3072) has constructed tables of corrections by interpolation from experimental data up to 220° for two kinds of thermometer graduated in degrees, and up to 100° for thermometers graduated in tenths of a degree. All these thermometers were constructed of Jena glass, and from the results it would appear that the form of the thermometer, and doubtless also the nature of the glass, have a notable influence on the magnitude of the correction.

The various parts of the simple apparatus (Figs. 1 and 2) may require modification under certain circumstances.

The still.—For larger quantities of liquid, a tin or copper vessel is preferable to glass.

The head.—The modifications of this part

T − t	N																				
	10	20	30	40	50	60	70	80	90	100	110	120	130	140	150	160	170	180	190	200
10	0·01	0·03	0·04	0·06	0·07	0·09	0·10	0·11	0·13	0·14	0·16	0·17	0·19	0·20	0·21	0·22	0·24	0·26	0·27	0·29
20	0·02	0·06	0·09	0·11	0·14	0·17	0·20	0·22	0·26	0·29	0·31	0·34	0·37	0·40	0·43	0·46	0·49	0·51	0·54	0·57
30	0·04	0·09	0·13	0·17	0·21	0·26	0·30	0·34	0·39	0·43	0·47	0·51	0·56	0·60	0·64	0·68	0·73	0·77	0·82	0·86
40	0·05	0·11	0·17	0·23	0·28	0·34	0·40	0·47	0·52	0·57	0·63	0·69	0·74	0·80	0·86	0·91	0·97	1·03	1·09	1·14
50	0·07	0·14	0·21	0·29	0·36	0·43	0·50	0·60	0·64	0·71	0·79	0·86	0·93	1·00	1·07	1·14	1·22	1·29	1·36	1·43
60	0·08	0·17	0·25	0·35	0·43	0·51	0·60	0·70	0·77	0·86	0·94	1·03	1·12	1·20	1·29	1·37	1·46	1·54	1·63	1·72
70	0·10	0·20	0·30	0·40	0·50	0·60	0·70	0·80	0·90	1·00	1·10	1·20	1·30	1·40	1·50	1·60	1·70	1·80	1·90	2·00
80	0·11	0·22	0·34	0·47	0·60	0·70	0·80	0·91	1·03	1·14	1·26	1·37	1·49	1·60	1·72	1·83	1·94	2·05	2·17	2·29
90	0·13	0·26	0·39	0·52	0·64	0·77	0·90	1·03	1·16	1·29	1·42	1·54	1·66	1·80	1·93	2·06	2·17	2·31	2·45	2·54
100	0·14	0·29	0·43	0·57	0·71	0·86	1·00	1·14	1·30	1·43	1·58	1·73	1·84	2·00	2·15	2·29	2·43	2·57	2·72	2·86
110	0·16	0·31	0·47	0·63	0·79	0·94	1·10	1·26	1·42	1·58	1·73	1·89	2·04	2·20	2·36	2·51	2·67	2·83	2·99	3·15
120	0·17	0·34	0·51	0·69	0·86	1·03	1·20	1·37	1·54	1·71	1·89	2·06	2·23	2·40	2·57	2·74	2·92	3·09	3·26	3·43

of the apparatus will be considered under *Fractional distillation.*

The condenser.—For very volatile liquids, the condensing tube must be cooled by ice or a freezing mixture (pounded ice and salt or ice and concentrated hydrochloric acid, &c.). In this case, a spiral or 'worm' tube should be used (Fig. 3). Condensation of moisture in the receiver is prevented by the drying tube *a*.

The receiver.—If a liquid boils at a very high temperature, or if it suffers decomposition at the ordinary boiling-point, it may be necessary to distil it under reduced pressure. For cases of simple distillation, the apparatus shown in Fig. 4 may be employed, but if the distillate is to be collected in separate portions, as in fractional distillation, the removal of the receiver would necessitate the admission of air into the apparatus and a fresh exhaustion after each change. This inconvenience may be obviated by the employment of stopcocks arranged in such a manner

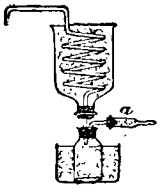


FIG. 3.

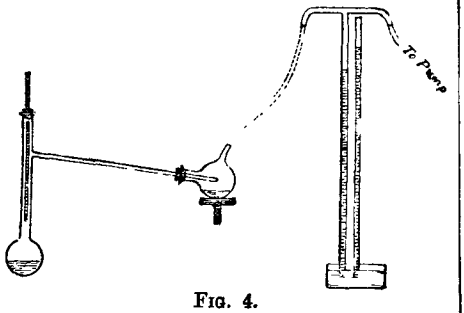


FIG. 4.

that air may be admitted into the receiver and a fresh one put in its place while the distillation bulb remains exhausted (Thörner, Ber. 9, 1868; F. D. Brown, Chem. Soc. Trans. 35, 554; L. T. Thorne, Ber. 16, 1327 (Fig. 5); Lothar Meyer, *ibid.* 20, 1834). Or again, a series of receivers on a revolving stand placed under an exhausted bell-jar may be employed (Gorboff

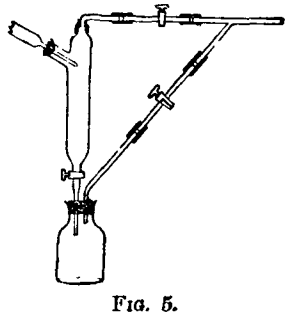


FIG. 5.

and Kessler, Ber. 18, 1363; Brühl, *ibid.* 21, 3339 (Fig. 6)).

Many liquids absorb moisture from the air or are acted upon by oxygen, and in these cases special precautions must be taken, the moist air in the apparatus being expelled and replaced by dry air, carbon dioxide, nitrogen, or hydrogen; the receivers must also be protected by drying tubes. (For example, *v.* Thorpe, Chem. Soc. Trans. 47, 120; Young, *ibid.* 59, 923.)

Theory of distillation. Investigations of the vapour pressures of liquids have thrown much light on the subject of distillation. If a pure liquid be confined in the space above the mercury in a barometer tube, it will evaporate until the pressure of its vapour—measured directly by the depression of the mercury column—has reached a definite amount, which, for a given substance, and, if liquid be still present, depends solely on the temperature. From the readings of pressure at various temperatures we may construct a curve to illustrate the relations of temperature to pressure for a given substance, but this curve has a twofold meaning, for it represents not only the vapour pressures at definite temperatures, but also the boiling-points of the liquid under definite pressures. Thus the vapour pressure of pure water at 100° is 760 mm. of mercury at 0°; and under a pressure of 760 mm. water boils at 100°. Again, the vapour pressure of water at 0° is 4·6 mm., and if the pressure in a distillation bulb containing water be reduced to 4·6 mm., the water will boil at 0°. The truth of this general statement was conclusively proved by Regnault (Mém. de l'Academie, 21 and 26).

Regnault also investigated the behaviour of a few mixed and heterogeneous liquids, which he

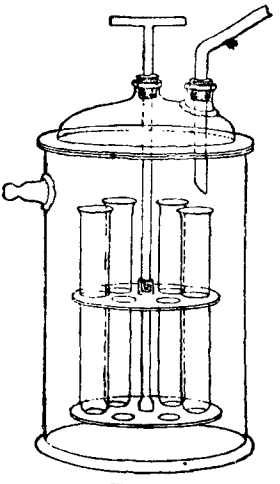


FIG. 6.

divided into three classes: (1) liquids which are quite or almost insoluble in each other; (2) liquids which are miscible only within certain limits; (3) liquids which mix in all proportions. Regnault employed both the statical and dynamical methods of investigation; that is to say, he determined, on the one hand, the vapour pressures of the liquids at various temperatures in the barometer tube, and, on the other hand, the boiling-points of the liquids under various pressures.

The behaviour of two liquids, A and B, when brought into contact with each other, must be affected (*a*) by the attraction of the like molecules; those of A for each other, and those of B for each other; and (*b*) by the mutual attraction of the molecules of A and B. If the attraction of the unlike molecules is relatively very slight, it may be expected that the liquids will be non-miscible, or nearly so, as in the case of benzene and water. If the attraction of the

unlike molecules is greater, but still relatively small, miscibility within limits may be expected, as, for example, with aniline and water. In such cases there is frequently slight expansion and slight absorption of heat on admixture. Comparing together various pairs of liquids, as the mutual attraction of the unlike molecules increases relatively to that of the like molecules, the following changes may be expected: (*a*) increasing and finally infinite miscibility; (*b*) slight expansion, diminishing to zero, and followed by increasing contraction; (*c*) diminishing absorption of heat, changing to increasing heat evolution. These changes do not, in many cases, run strictly *pari passu*, and among liquids which are miscible in all proportions, it is not unusual to find a small amount of contraction attended by a slight absorption of heat, as, for example, when a little water is added to normal propyl alcohol, but when certain compounds, such as chlorobenzene and bromobenzene, which are chemically closely related, are mixed together, there is no appreciable change of volume or temperature. For such substances it is probable that the different molecular attractions, A for A, B for B, and A for B, are very nearly equal, and that the relation suggested by Galitzine (Wied. Ann. 41, 770; and by D. Berthelot, Compt. rend. 126, 1703), namely, that $a_{A.B}=\sqrt{a_A.a_B}$, holds good, where $a_{A.B}$ represents the attraction of the unlike molecules, and a_A and a_B the respective attractions of the like molecules.

It would appear, then, that there are two very simple cases; I. that in which the liquids are non-miscible; II. that of two infinitely miscible and closely related liquids which show no heat or volume change on admixture.

I. It was found by Regnault that when two non-miscible liquids are placed together over the mercury in a barometer tube, the observed vapour pressure is equal to the sum of the vapour pressures of the two liquids when heated separately to the same temperature. It is only necessary that both substances should be present in sufficient quantity, and that the tube should be shaken or sufficient time allowed for the evaporation of the heavier liquid. The liquids evaporate independently of each other, and Dalton's law of partial pressures is therefore applicable to the distillation of non-miscible liquids. Each vapour behaves to the other as an indifferent gas, and the boiling-point of each liquid depends on the partial pressure of its own vapour. The temperature is necessarily the same for both liquids, and the total pressure, if the distillation is carried out in the ordinary manner, is equal to that of the atmosphere. The boiling-point is, therefore, that temperature at which the sum of the vapour pressures of the components is equal to the atmospheric pressure. For example, at 90·23° the vapour pressure of water is 530·1 mm.; and that of chlorobenzene is 210·1 mm.; total, 740·2 mm.; and it was found that when chlorobenzene and water were distilled together under a barometric pressure of 740·2 mm., the temperature varied only between 90·25° and 90·35°, until there was scarcely any chlorobenzene left in the residue, when it rose rapidly to 100°. The boiling-point of a pair of non-miscible liquids is necessarily lower than that of the more volatile component, and may be far lower than that of the less volatile.

The process of distillation with steam is very frequently employed in the case of substances of high boiling-point, which are insoluble or only slightly soluble in water, such as aniline or nitrobenzene. (For the application of steam distillation to the preparation of ethereal oils, *v.* von Rechenberg, Theorie der Gewinnung und Trennung der ätherischen Oele durch Destillation, Schimmel & Co. 1910.)

The composition of the vapour—and therefore of the distillate—from two non-miscible liquids, like the vapour pressure and boiling-point, is independent of the relative amounts of the components, provided that both are present in sufficient quantity and that evaporation can take place freely. Calling the vapour densities D_A and D_B, and the vapour pressures at $t°$ p_A and p_B, there will be, in a litre of the mixed vapour, 1 litre of A at $t°$ and p_A mm., and 1 litre of B at $t°$ and p_B mm. The weights of vapour will therefore be:

$$\frac{0{\cdot}0899\times D_A\times 273\times p_A}{(273+t)\times 760} \text{ and } \frac{0{\cdot}0899\times D_B\times 273\times p_B}{(273+t)\times 760}$$

respectively, and the relative weights will be $\frac{D_A\times p_A}{D_B\times p_B}$ (Naumann, Ber. 10, 1421, 1819, 2014, 2099; Brown, Chem. Soc. Trans. 35, 547).

The vapour density of chlorobenzene is 56·2, and that of water is 9; and at 90·23° the relative weights of vapour will be

$$\frac{m'_A}{m'_B}=\frac{56{\cdot}2\times 210{\cdot}1}{9\times 530{\cdot}1}=2{\cdot}475,$$

and the percentage weight of chlorobenzene will be 71·2. In the actual experiment to which reference has been made, the percentage of chlorobenzene in the distillate was found to be 71·4. Both boiling-point and vapour composition agree well with the calculated values.

II. The vapour pressure of a mixture of two infinitely miscible liquids which are chemically closely related to each other, or, probably, for which $a_{A.B}=\sqrt{a_A.a_B}$, is given by the formula $100p = \text{M}p_A+(100-\text{M})p_B$, where M is the molecular percentage of A, and p, p_A, and p_B are the vapour pressures of the mixture and of A and B respectively, at the same temperature, $t°$. In other words, the relation between vapour pressure and molecular composition is represented by a straight line (Van der Waals, Proc. Roy. Acad. Amsterdam, 3, 170; Young, Chem. Soc. Trans. 81, 768; Young and Fortey, *ibid.* 83, 45; Zawidski, Zeitsch. physikal. Chem. 35, 129). The relation has been found to hold accurately for chlorobenzene and bromobenzene, and with very slight error for other pairs of closely related liquids.

In order to calculate the boiling-points of all mixtures of two such liquids under a given pressure, p, the vapour pressures of each must be known at all temperatures between their respective boiling-points under that pressure. The percentage molecular composition of mixtures which would exert the vapour pressure

p must then be calculated at a series of temperatures between these limits by means of the formula $M = 100\frac{p_B - p}{p_B - p_A}$. Lastly, the values of M must be plotted against the temperatures, when the curve drawn through the points will give the required relation between boiling-point and molecular composition. In the cases examined, the agreement between the observed and calculated results is quite satisfactory.

The relation between the composition of a liquid mixture and that of its vapour (distillate) has been the subject of many experimental investigations (Brown, Chem. Soc. Trans. 35, 547; 39, 304; Lehfeldt, Phil. Mag. (v.) 46, 42; Zawidski, Zeitsch. physikal. Chem. 35, 129; Carveth, J. Phys. Chem. 3, 193; Winkelmann, Wied. Ann. 39, 1; Linebarger, J. Amer. Chem. Soc. 17, 615; Gahl, Zeitsch. physikal. Chem. 33, 179; Rosaneff, Lamb, and Breithut, *ibid.* 66, 349; Rosanoff and Easley, J. Amer. Chem. Soc. 31, 953); for a description of which (up to the year 1903, *v.* Young's Fractional Distillation, 71-113). Unfortunately, however, it is only in a very few cases that the mixtures investigated consisted of closely related liquids. In the discussion of their results, Lehfeldt and Zawidski made use of formulæ which they derived from a general equation proposed independently by Duhem and by Margules, and it is to be noted that both formulæ, in the simplest cases, can be reduced to one originally given by Brown, $\frac{m'_A}{m'_B} = c\cdot\frac{m_A}{m_B}$, where m'_A and m'_B are the relative weights of the two substances in the vapour, m_A and m_B the relative weights in the liquid, and c is a constant. From Zawidski's formula it would follow that $c = \frac{p_A}{p_B}$. So far as experimental evidence is available, it would appear that Brown's formula is applicable to mixtures of liquids for which $a_{A\cdot B} = \sqrt{a_A \cdot a_B}$, and that for closely related liquids $c = \frac{p_A}{p_B}$.

When the components of a liquid mixture are not chemically closely related, the relation between vapour pressure and molecular composition is not, as a rule, represented by a straight line, but by a curve, and, in all probability, the form of the curve depends on the relation between $a_{A\cdot B}$ and $\sqrt{a_A \cdot a_B}$, as shown in Fig. 7. That is to say, when

$$a_{A\cdot B} < \sqrt{a_A \cdot a_B}, 100p > Mp_A + (100 - M)p_B,$$

and *vice versa*.

The greater the difference between $a_{A\cdot B}$ and $\sqrt{a_A \cdot a_B}$ the greater will be the curvature; and it will be seen that, for any given values of p_A and p_B, if the deviation from straightness exceeds a certain limit, there must be a point of maximum or minimum pressure on the curve. It is obvious, also, that the smaller the difference between p_A and p_B, the smaller will be the deviation required to give a maximum or minimum pressure. If $a_{A\cdot B}$ is so much smaller than $\sqrt{a_A \cdot a_B}$ that the two liquids are only partially miscible, the maximum pressure will not be represented by a single point, but by a horizontal line forming part of the curve.

The influence of chemical relationship is well seen by the behaviour of the monhydric aliphatic alcohols towards water. These alcohols may be regarded as derivatives of water, formed by the replacement of a hydrogen atom by the group C_nH_{2n+1}; the smaller the alkyl group, the closer is the relationship of the alcohol to water. At the ordinary temperature methyl alcohol is miscible with water in all proportions, as also are ethyl and propyl alcohols; normal butyl and *iso*butyl alcohol are only partially miscible with water; and the solubility of the higher alcohols in water diminishes with rise of molecular weight, cetyl alcohol, for example, being practically insoluble. The volume and heat changes on admixture with water similarly indicate that the attraction of the unlike molecules diminishes as the molecular weight of the alcohol increases. Lastly, the deviation of the vapour pressure curves from straightness increases (Konowalow, Wied. Ann. 14, 34), as may be seen from Fig. 8.

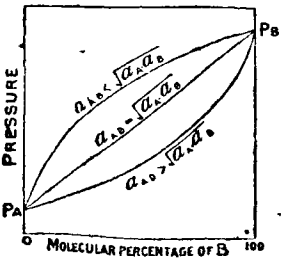


FIG. 7.

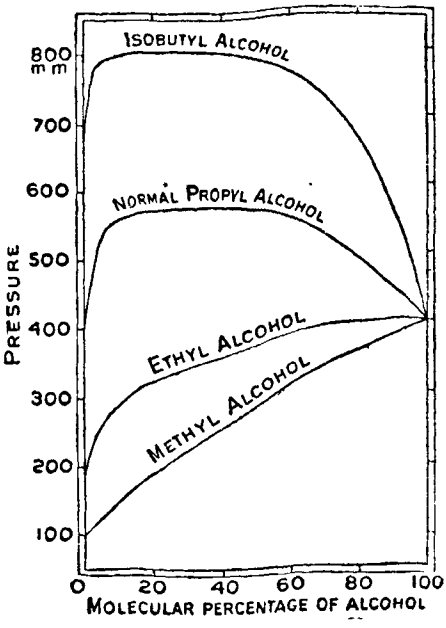


FIG. 8.

(The temperatures are such that the vapour pressure of each pure alcohol is 400 mm.)

The boiling-points of liquids which are not closely related cannot, as a rule, be calculated by means of the formula $M = 100\frac{p_B - p}{p_B - p_A}$. If, as is usually the case, the vapour pressures of the mixtures are higher than are given by the

formula $100p = Mp_A + (100 - M)p_B$, the observed boiling-points will be lower than the calculated; if the vapour pressures are lower, the boiling-points will be higher. Moreover, when there is a point of maximum pressure on the curve which shows the relation between vapour pressure and molecular composition, there must be a point of minimum temperature on the boiling-point—molecular composition curve, the composition of the mixture which exerts a maximum vapour pressure, p, at $t°$ being the same as that of the mixture which has the miniumm boiling-point, $t°$, under the pressure p. So, also, two substances capable of forming a mixture of minimum vapour pressure can also form a mixture of maximum boiling-point.

Such mixtures of either minimum or maximum boiling-point, when distilled, boil at a constant temperature without change of composition, like pure substances, and they have frequently been mistaken for chemical compounds. The composition, however, depends on the pressure, which would not be the case with a definite compound; and, moreover, mixtures of minimum boiling-point are formed owing to the relatively *small* attraction of the unlike molecules for each other. A very striking example of the influence of pressure on the composition of the mixture of constant boiling-point has recently been observed by Wade in the case of ethyl alcohol and water. Under normal pressure the mixture of minimum boiling-point contains 4·43 p.c. of water. At higher pressures the percentage of water is slightly higher; at lower pressures it is smaller, and it is remarkable that the diminution in the percentage of water becomes more and more rapid as the pressure falls, so that below 80 mm. no mixture of minimum boiling-point is formed at all.

In the case of three liquids, if each of the three possible pairs is able to form a mixture of minimum boiling-point, it may happen that a particular mixture of all three liquids will boil constantly at a lower temperature than will any of the pairs or single liquids. Thus benzene and water form such ternary mixtures of minimum boiling-point with ethyl, *n*-propyl, *iso*propyl, and tertiary butyl alcohols (Young, Chem. Soc. Trans. 81, 707; Fortey and Young, *ibid.* 81, 739).

A table of mixtures of constant boiling-point is given in Young's Fractional Distillation, 67–69. Other mixtures have since been discovered by Wade (Chem. Soc. Trans. 85, 938; 87, 1656; *v.* also 95, 1842).

The composition of the vapour from a mixture of liquids which are not closely related, cannot, as a rule, be calculated from the vapour pressures of the components and the composition of the liquid, but for purposes of interpolation the formulæ of Lehfeldt or Zawidski may be found useful (*l.c.*).

Fractional distillation. It has been stated that Brown's formula, $\frac{m'_A}{m'_B} = c\frac{m_A}{m_B}$, is applicable to mixtures of all closely related liquids so far investigated, and that, in all probability, $c = \frac{p_A}{p_B}$. The value of c is necessarily such that the vapour is richer than the liquid in the more volatile component. The first portion of distillate obtained by condensation of the vapour will, therefore, be richer, and the residual liquid will be slightly poorer in that component. Continuing the distillation, the vapour evolved from the residual liquid will again be richer than the liquid in contact with it in the more volatile component, though poorer than the first portion of vapour. If successive portions of vapour be condensed, the percentage of the more volatile component in the distillates or *fractions* will steadily diminish, until, if the constant c differs greatly from unity, the residue will consist of the less volatile liquid in a pure or very nearly pure state. As the distillation proceeds, the temperature will, therefore, rise until, if c has a high value, the boiling-point of the less volatile component is reached.

If the fractions obtained in the first distillation were redistilled, each of them could be separated into smaller fractions, the first richer and the last poorer in the more volatile component, and by a process of systematic fractional distillation it should, theoretically, be possible to effect a separation of both components.

A mathematical and experimental investigation (Barrell, Thomas, and Young, Phil. Mag. (v.) 37, 8) of the behaviour on distillation of mixed liquids which follow Brown's law, showed that with two components it is the liquid of higher boiling-point which is the easier to separate; and that if there are three or more components boiling at fairly equal intervals of temperature, the substances of intermediate boiling-point are the most difficult to separate, and the least volatile substance is the easiest.

The method employed for the fractional distillation of a mixture of two liquids can best be explained by taking a concrete example. A mixture of 100 grams of benzene (b.p. 80·2°) and 100 grams of toluene (b.p. 110·6°) was slowly distilled, and the distillate was collected in a convenient number of fractions, the receivers being changed when the boiling-point reached certain definite previously arranged temperatures, the actual readings being corrected for barometric pressure and for errors in the thermometer scale. The results of the first four fractionations, and also of the ninth, are given in Table I., next page.

In the first distillation the temperature rose almost at once to 86° (corr.), and the first portion of distillate was therefore collected in receiver 4. On the other hand, the temperature reached 110·6° before the whole of the liquid had come over; the residue, therefore, consisted of pure toluene.

The distillate in receiver 4 was now placed in a smaller flask and distilled, fractions being collected in receivers 2, 3, and 4. When the temperature reached 89·2°, the flame was removed, and the contents of receiver 5 were added to the residue in the still. The distillation was recommenced, and fractions were collected in receivers 3, 4, and 5, the flame being removed when the temperature reached 92·2°. The distillation was continued in a similar manner until, after addition of the contents of receiver 12, the temperature rose to 110·6°, when the residue of pure toluene was added to that from the first fractionation. The third and fourth fractionations were carried out like

TABLE I.

Number of receiver	Final temperature (corrected) = t	Weight of fraction = ΔW				t	ΔW
		I.	II.	III.	IV.	IX.	
Pure benzene	° —	—	—	—	—	80·2	10·20
1	81·2	—	—	12·95	31·55	80·3	45·00
2	83·2	—	3·80	24·80	23·90	80·6	17·55
3	86·2	—	33·85	22·75	16·20	81·4	7·20
4	89·2	9·75	22·30	13·50	9·55	83·5	4·50
5	92·2	51·80	19·65	11·80	8·00	88·0	3·30
6	95·4	28·85	13·60	9·15	5·80	95·4	2·75
7	98·6	21·20	12·95	7·30	5·35	102·8	2·60
8	101·6	12·80	9·05	6·75	4·65	107·3	2·85
9	104·6	11·45	8·90	6·30	3·85	109·4	3·15
10	107·6	14·15	10·80	7·95	5·85	110·2	3·45
11	109·6	13·45	9·60	8·95	7·40	110·5	7·00
12	110·6	24·90	30·75	33·05	30·50	110·6	5·75
Pure toluene	(110·6)	10·90	22·95	31·35	42·10	(110·6)	72·10

the second. In the subsequent fractionations the temperature ranges of the middle fractions were gradually increased and those of the lowest and highest fractions diminished. It was not until the ninth fractionation that pure benzene began to be collected. Eventually 81·4 grams of pure benzene and 88·8 grams of pure toluene were recovered.

Full details of the systematic fractional distillation of mixtures of two liquids and three liquids, and of more complex mixtures, are given in 'Fractional Distillation,' 114–143.

If the components of a mixture are not closely related, the composition of the vapour cannot, as a rule, be calculated by Brown's formula, but even in such cases the percentage of the more volatile component in the vapour will be greater than in the liquid, and the separation by fractional distillation is theoretically possible, unless the deviation of the vapour pressure-composition curve from straightness is so great that a mixture of maximum or minimum vapour pressure is formed.

For mixtures to which Brown's law is applicable, it may be stated quite generally that the greater the difference between the boiling-points of the compounds, the more readily can a separation be effected by fractional distillation, but for other mixtures the form of the curve representing the relation between boiling-point and molecular composition, if known, must be taken into account. If the

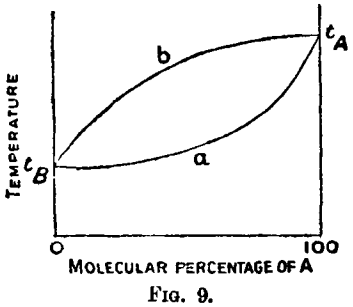


FIG. 9.

curve for two components were of the form *a* (Fig. 9), the substance of higher boiling-point could be separated very easily, but the more volatile component only with great difficulty, if at all. On the other hand, if the curve were of the form *b*, nearly horizontal at the higher temperature, the more volatile component would be comparatively easy, and the less volatile difficult to separate. The first case is frequently met with, the second seldom. With curves of the form *c* and *d* (Fig. 10) it would not,

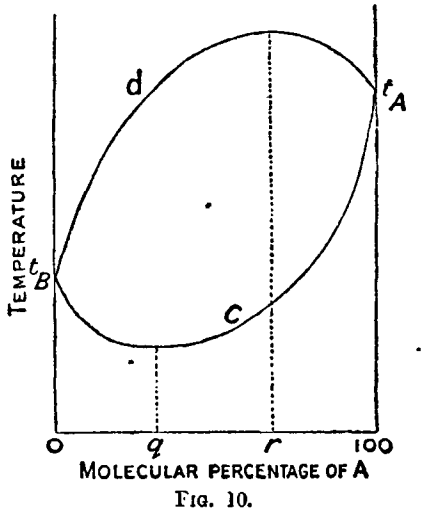


FIG. 10.

under any conditions, be possible to separate both components by distillation of any given mixture, but it would be possible to separate the mixture of minimum or maximum boiling-point from that component which was in excess. In a case represented by curve *c*, where the minimum temperature corresponds to the molecular composition *q*, the distillation might proceed in either of three ways: (1) If the liquid mixture had the composition *q*, it would distil unchanged in composition at the constant minimum temperature; (2) if the molecular percentage of A were less than *q*, the liquid would tend to separate into two components, the more volatile of which would be the mixture

of minimum boiling-point, and the less volatile the substance B; (3) if the molecular percentage of A were greater than *q*, the components separable by listillation would be, first, the mixture of minimum boiling-point, and, second, the liquid A. A well-known case of this kind is that of normal propyl alcohol and water; the boiling-points under normal pressure are: water, 100°; *n*-propyl alcohol, 97·2°; mixture of minimum b.p. 87·7°. This mixture contains 43·2 molecules p.c. of the alcohol; it was described for many years as a hydrate of propyl alcohol. If the curve had the form *d*, the mixture would distil like a pure liquid if it had the composition *r*, or it would tend to separate into two components, the first being either A or B, according as the molecular percentage of A in the original mixture was greater or less

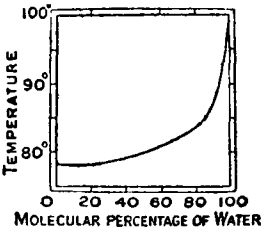


FIG. 11.

than *r*, and the second the mixture of maximum boiling-point. Formic acid and water behave in this manner, as shown by Roscoe (Chem. Soc. Trans. 13, 146; 15, 270). Boiling-points: water, 100°; formic acid, 99·9°; mixture of maximum b.p., 107·1°; molecular percentage of acid in mixture, 56·7°.

If, as with ethyl alcohol and water (Fig. 11), the mixture of constant boiling-point distils at nearly the same temperature as one of the two pure liquids, it is impossible to separate that liquid in a pure state by distillation. In this case, as the curve is exceedingly flat at the lower temperature (Noyes and Warfel, J. Amer. Chem. Soc. 23, 463), it is practically impossible to separate the mixture of minimum boiling-point (containing 4·43 p.c. by weight of water) in a pure state even when water is in excess, although it is quite easy to separate pure water from dilute spirit.

The correct interpretation of the results of the fractional distillation of a complex mixture may be rendered very difficult by the following causes: (1) the presence of two components boiling at nearly the same temperature; (2) the presence of one or more components in relatively very small quantity; (3) the formation of mixtures of constant boiling-point. It is only by plotting the total weights of distillate against the temperatures, or by dividing the weight of each fraction, Δw, by its temperature range and tabulating the ratios $\Delta w/\Delta t$, that the results are likely to be understood, and in any case, the existence of a mixture of constant boiling-point may not be discovered, and it may be difficult to decide whether a distillate collected at a practically constant temperature consists of a single pure substance or of two liquids boiling at nearly the same temperature.

All the above difficulties are met with in the fractional distillation of petroleum, which contains homologous and isomeric paraffins, polymethylenes and their alkyl derivatives (naphthenes) and aromatic hydrocarbons, Russian petroleum being relatively rich, and American petroleum poor in naphthenes and aromatic hydrocarbons. When American petroleum was carefully distilled, it appeared at first as though the distillate coming over between the ordinary temperature and 40° contained only a single component, boiling at about 33°; but by systematic fractional distillation with a very efficient still-head, it became evident (Fig. 12) that two components, *iso*pentane, b.p. 27·95°, and normal pentane, b.p. 36·2°, were present (Young, Chem. Soc. Trans. 71, 440). Again, in the early fractionations there appeared to be no indication of the presence of any component boiling between 40° and 60°, but by tabulating the values of $\Delta w/\Delta t$, it was seen that a very small quantity of a liquid boiling at about 50° was present, and a distillate coming over almost constantly at 49·5° was eventually obtained. A chemical and physical investigation of this distillate showed, however, that it was a mixture of pentamethylene and a hexane of low boiling-point. The presence of benzene in American petroleum is indicated by the formation of dinitrobenzene, when the distillate from, say, 60° to 80° is treated with nitric and sulphuric acids (Schorlemmer, Annalen, 127, 311). But when the petroleum was carefully fractionated, it was found that the small fraction coming over at about 80° yielded no dinitrobenzene, the greater part being obtained from the fractions below 70°. This anomaly is explained by the fact that benzene forms a mixture of constant

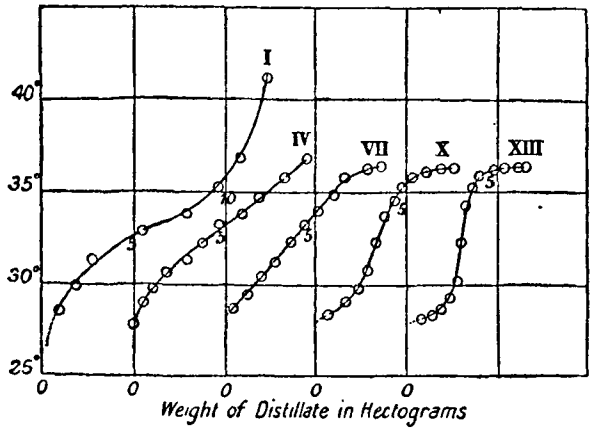


FIG. 12.

boiling-point with *n*-hexane, coming over at almost the same temperature as the paraffin. The amount of benzene being relatively small,

the whole of it distils over at the low temperature. In Russian petroleum the percentage of benzene is so much greater that some of it comes over at its true boiling-point, 80·2° (Young, Chem. Soc. Trans. 73, 905).

(For a detailed discussion of the interpretation of the results of the fractionation of complex mixtures, *v.* Fractional Distillation, chap. 19.)

Improved still-heads. It would be quite impossible to effect really difficult separations by means of the ordinary apparatus employed for distillation, and various modifications of the still-head have been devised in order to increase its efficiency. Even when the separation is an easy one, much time and material may be saved by the employment of efficient still-heads. Great progress was made in the improvement of the still-head in commerce—notably for the better separation of alcohol from weak spirit—before any advance was made in the laboratory. It will, however, be more convenient to consider first those forms of apparatus which are suitable for laboratory purposes.

In choosing or constructing a still-head, the first point to be considered is its efficiency in separating the components of a mixture. It frequently happens, however, that the quantity of liquid available is small, and it is therefore important that the quantity of condensed liquid in the still-head at any moment shall be as small as possible. If the residual liquid is of value, it is also of importance that the condensed liquid in the still-head shall all return to the still after the source of heat is removed.

In comparing the efficiency and usefulness of different still-heads, it is necessary always to distil a mixture of the same composition; and the rate of distillation must always be the same, because the efficiency of any still-head is greatly diminished by increasing the rate. In the comparisons mentioned in this article, equal weights of pure benzene and pure toluene were employed, and the distillate was collected at the rate of one drop per second. Unless otherwise stated, 50 grams of the mixture were distilled.

Of all possible forms, the plain vertical still-head is the least efficient. During distillation, as the vapour rises up the cylindrical tube, the outer part of it comes in contact with the condensed liquid flowing down the sides of the tube. Since the tube is constantly losing heat by radiation and by conduction to the surrounding air, this liquid is constantly cooled and fresh condensation constantly goes on, the outermost layer of vapour probably condensing almost completely with little change of composition. The central portion of vapour rises rapidly up the tube, and can only reach the liquid by diffusion or by convection currents, and much of it may pass through the still-head without reaching the liquid at all; the condensed liquid, on the other hand, flows rapidly back to the still. In order, however, that a satisfactory separation of the components may take place, as much of the vapour as possible should come in contact with the hot condensed liquid, so that equilibrium, as regards composition, may be brought about all through the tube.

The efficiency of a plain vertical still-head is, roughly, proportional to its length. For tubes of equal length the efficiency is lowest when the internal diameter is about 14 mm. On the other hand, the quantity of liquid and vapour in the still-head increases regularly with the width of the tube; it is therefore better to use very narrow rather than very wide tubing.

Better contact between liquid and vapour, and therefore greater efficiency, is ensured by sloping the middle part of the tube, the extremities being kept vertical, and the efficiency is further improved by bending the sloping portion so as to form a spiral. In Young's 'rod and disc' still-head (Fig. 13), the downflow of part of the condensed liquid is greatly retarded by the discs on the central glass rod, and this liquid is protected from the cooling action of the air; at the same time, eddies and cross-currents are produced in the vapour. The increase in efficiency caused by the introduction of the easily constructed rod with discs is very marked. Wurtz (Ann. Chim. Phys. iii. 42, 129) recommended a vertical tube with a series of bulbs blown on it, and Young has shown that the efficiency is somewhat increased and the amount of liquid in the still-head is greatly diminished by blowing pear-shaped instead of spherical bulbs on the tube (Fig. 14). The 'rod and disc' and 'pear' still-heads are specially suitable for liquids of high boiling-point.

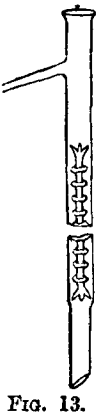


FIG. 13.

Greater efficiency, combined with diminished condensation of liquid in the still-head, is attained in Young's 'evaporator' column, one section of which is shown in Fig. 15. The

FIG. 14.

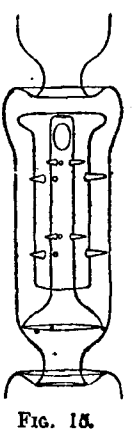


FIG. 15.

vapour rises up the inner tube, passes down between the inner and middle tubes, and up again between the middle and outer tubes, and so reaches the section above. The liquid condensed in the upper part of the still-head falls in drops from the depression at the top of the section on to the flattened top of the inverted middle tube, and spreads itself over its surface, falling again in drops from the bottom of this tube. The temperature of the vapour passing

through the inner tube of any section being higher than the boiling-point of the condensed liquid falling on to the inverted tube, re-evaporation takes place to some extent, and, if there is much difference between the boiling-points of the components of the mixture being distilled, ebullition may actually occur. The quantity of condensed liquid in the still-head is thereby greatly reduced. The 'evaporator' still-head is specially suitable for accurate work where great efficiency is required (Chem. Soc. Trans. 75, 679).

The 'Hempel' still-head (Zeitsch. anal. Chem. 20, 502) consists simply of a wide vertical tube, filled with glass beads of special construction, and constricted below to prevent the beads from falling out. A short, narrower vertical tube with side delivery tube is fitted by means of a cork into the wider tube. The advantages of the Hempel apparatus are simplicity and efficiency, but the amount of liquid in the still-head is excessive.

The results obtained with various still-heads are given in Table II.

TABLE II.

Nature of still-head or dephlegmator	Plain vertical, 5·1 mm. diameter	Plain vertical 14·0 mm. diameter	Plain vertical 25·7 mm. diameter	'Rod and disc' 14 mm. diameter	'Pear'	'Evaporator'	'Evaporator'	'Evaporator'	'Hempel' with 200 beads	Glinsky	Le Bel-Henninger	Young and Thomas	Young and Thomas
Number of discs, bulbs, or sections	-	—	—	20	13	3	5	8	—	3	3	3	18
Vertical height in cm.	62	62	62	62	62	46	62	78	58	30	43	51[1]	130
Final temperature of fraction	Percentage weight of distillate												
83·2	—	—	—	1·4	3·0	12·80	26·00	35·85	20·6	1·1	0·5	0·6	38·8
86·2	0·5	0·1	0·2	18·1	26·2	21·15	12·35	6·50	15·4	11·7	17·8	21·8	4·1
89·2	22·2	12·8	20·0	15·8	11·0	7·50	5·60	2·90	7·2	17·3	15·9	14·3	1·9
92·3	16·5	21·5	18·8	9·7	5·8	4·80	3·25	2·15	3·4	11·9	8·8	7·8	1·8
95·4	9·2	11·0	9·2	6·1	5·2	3·35	1·95	1·40	3·2	7·5	7·2	5·0	1·3
98·5	7·2	8·9	7·2	4·2	2·4	2·70	1·30	1·15	2·2	5·6	4·3	4·7	1·2
101·6	5·8	7·4	4·7	3·8	2·4	2·30	1·80	1·05	1·8	5·7	4·8	4·0	0·9
104·6	5·5	6·2	5·9	4·2	2·8	2·50	1·50	1·15	2·9	5·6	4·6	3·6	1·2
107·6	5·9	7·3	6·4	4·3	3·6	3·50	2·45	1·60	3·2	8·9	5·5	5·2	2·0
110·0	7·1	8·4	10·0	8·0	5·0	6·50	4·20	3·95	6·8	13·7	9·8	7·3	4·0
110·6	8·9	9·0	7·2	6·6	11·0	10·50	11·40	9·60	8·4	2·5	6·8	9·8	8·1
Pure toluene by difference	11·2	7·4	10·4	17·8	21·6	22·40	27·90	32·70	24·9	8·5	14·0	15·9	34·7
Weight of liquid and vapour in still-head	1·05	1·55	3·15	2·35	2·6	2·70	4·55	6·25	7·85	2·8	5·85	2·8	12·1

In many of the still-heads employed on the large scale, for example in the Coffey still (Fig. 28), the condensed liquid is caused, by means of suitable obstructions, to collect into shallow pools, and the ascending vapour has to force its way through these pools; very good contact is thus brought about between vapour and liquid at definite intervals. The excess of liquid is carried back from pool to pool, and finally to the still by suitable trapped reflux tubes. It is convenient to reserve the term 'dephlegmator' for this class of still-head. The 'Le Bel-Henninger' (Fig. 16) and the 'Glinsky' (Fig. 17) dephlegmators have been very frequently employed for laboratory work, but they do not give good results when small quantities of liquid are distilled; the dephlegmators of Brown (Chem. Soc. Trans. 37, 49) (Fig. 18) and of Young and Thomas (*ibid.* 75, 679) follow the principle of the Coffey still more closely, and are much better in this respect.

In a comparison of the Glinsky, Le Bel-Heßninger, and Young and Thomas dephlegmators, each with three sections, it was found that when 400 grams of the mixture of benzene and toluene were distilled, there was not a great difference in efficiency, but the Glinsky was the least satisfactory. With 50 grams of the mixture the differences (Table II.) were quite noticeable, and with 25 grams they were greatly accentuated. With the Glinsky column the highest temperature reached was only 107·6°, and the residue, when distilled from a very small bulb, came over between 102·2° and 110·4°. No pure toluene was therefore obtained, and the residue left in the still was distinctly less pure than the last portion of distillate collected. With the Le Bel-Henninger column the highest temperature was only 107·35°, and the residue began to boil at 105·7°; with the Young and Thomas column the temperature just reached 110·6°, and the residue

[1] Unnecessarily long.

began to boil at 110·4°. The 'rod and disc,' the 'pear,' and the 'evaporator' still-heads gave better results when only 25 grams of the mixture were distilled, the residue in each case consisting of pure toluene. These results show that for small quantities of liquid the Young and Thomas dephlegmator gives much better results than the Glinsky or Le Bel-Henninger, but that none of them is so satisfactory as the other still-heads.

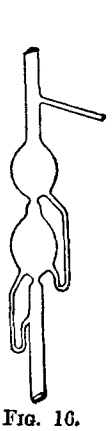


FIG. 16.

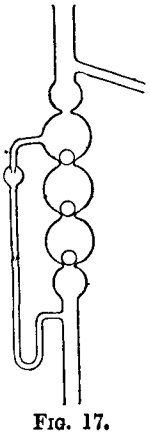


FIG. 17.

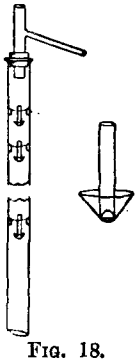


FIG. 18.

In order that a dephlegmator may give the best results, the following requirements should be fulfilled: 1. It should be possible to greatly increase the number of sections without seriously increasing the fragility of the apparatus. 2. As the amount of condensed liquid flowing back at any level is greatest at the bottom and least at the top, it follows that, in order to form a pool, more complete obstruction is required at the top of the column than at the bottom. 3. Since the amount of condensed liquid in the still-head should be as small as possible consistently with efficiency, the reflux tubes should not be wider—in that part which is filled with liquid during distillation—than is necessary to carry back the liquid freely, and the traps should be no deeper than is required to prevent the ascending vapour from forcing its way through them. On the other hand, the upper part of the reflux tubes should be wide, so as to facilitate the entrance of the liquid. 4. There should be a rapid flow of condensed liquid through the reflux tubes, otherwise the change in composition of the liquid in these tubes will lag behind that of the distillate. 5. There should be a reflux tube connecting each section with the one below it, so that the change in composition may be regular from top to bottom of the column. In this respect the Glinsky dephlegmator is entirely wrong in principle. 6. When the distillation is completed, the residual liquid should return as completely as possible from the still-head to the still. In this respect the dephlegmators as a class are less satisfactory than the other still-heads.

By surrounding the still-head with water or any other liquid, the temperature of which is kept as little above the boiling-point of the more volatile component as will allow of vapour passing through, a considerable improvement in the separation is effected. The temperature of the bath, however, requires very careful regulation if the boiling-points of the components are near together, or if one component is present in large excess, for in either case a fall of a fraction of a degree would cause complete condensation of the vapour, while a slight rise of temperature would prevent any condensation from taking place, and there would be no fractionation whatever. In constructing a regulated temperature still-head, it is advisable to bend the tube into the form of a spiral, because its effective length may thus be greatly increased without unduly adding to the height of the bath, and also because the spiral form is more efficient than the vertical. This class of still-head was first recommended by Warren (Annalen, Suppl. 4, 51). A better apparatus was described by Brown (Chem. Soc. Trans. 37, 49; 39, 517) (Fig. 19). A combination of a regulated temperature still-head and dephlegmator was employed by Young and Thomas (*ibid.* 71, 440) for the separation of normal and *iso*-pentane from petroleum.

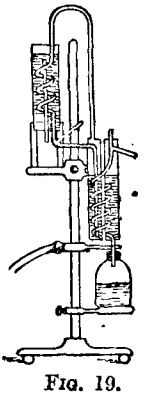


FIG. 19.

Experiments to test the relative efficiency of these various forms of apparatus have been made by Kreis (Annalen, 224, 259; Claudon, Bull. Soc. chim. 42, 613; Brown, Chem. Soc. Trans. 37, 49; Young, *ibid.* 75, 679; Fractional Distillation, chaps. 10, 11, and 14).

Continuous distillation of wort has long been carried out on the large scale by means of the Coffey still (Fig. 28). In 1902 Carveth (J. Phys. Chem. 6, 253) and Lord Rayleigh (Phil. Mag. vi. 4, 521) independently suggested apparatus intended for use in the laboratory. The liquid to be distilled (or its vapour) is introduced continuously into the middle part of a long spiral or other still-head, the lower part of which is prevented, by means of a liquid or vapour-bath, from cooling below the boiling-point of the less volatile of the two components, while the temperature of the upper part is prevented, by means of a liquid bath, from rising above the boiling-point of the more volatile component. Lord Rayleigh obtained good results in the distillation of weak spirit. It is probable that the method might be made applicable to the distillation of mixtures of three components (Fractional Distillation, 189).

As many of the stills used in the arts are described under the headings ALCOHOL, BENZENE, PARAFFIN, &c., it will be unnecessary here to give a minute description of all of them, but an account of the principles underlying the different methods will not be out of place.

The still is usually made of copper or some other metal, but for special purposes other materials must be employed. Thus for the distillation of sulphuric acid, vessels of glass or platinum are used; for nitric acid, cast iron is found to be the best material; stoneware or glass stills are employed for bromine and iodine; and so on.

The still may be heated by the free flame of a furnace or by steam. Fig. 20 shows an

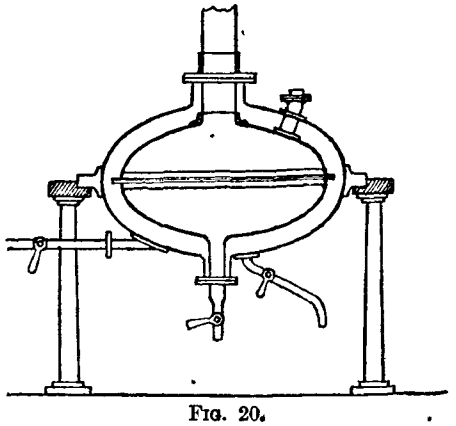


FIG. 20.

arrangement for heating a still with steam, which may be above the atmospheric pressure.

When only a rough separation of the constituents of a complex mixture is required, as in the preliminary distillation of coal tar, dephlegmators or rectifiers are not employed, but the vapours pass directly from the still to the condenser.

For the better separation of the components of a mixture, modified still-heads are employed. A simple apparatus, devised by Mansfeld for the distillation of tar oils, is shown in Fig. 21; the vapours are partially condensed in the still-head

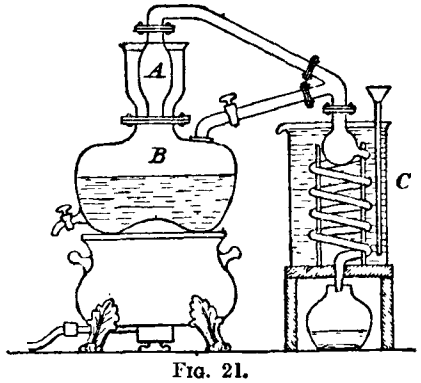


FIG. 21.

A, which is cooled by water, and the condensed liquid flows back into the still B, the purified vapour passing on to the condenser C.

A more perfect separation is effected by Coupier's apparatus (Fig. 22). In addition to the column A, there is a series of bulbs, B, B, placed in a cistern containing brine, which may be heated by steam by means of the pipe C. The vapour—of benzene, for example—partially freed from less volatile substances in the column, is further purified by partial condensation in the bulbs, the condensed liquid flowing back by the tubes D, D into the column, while the purified vapour passes on to the condenser by the pipe E.

A very similar arrangement is seen in the French column apparatus (Fig. 23). The liquid is heated by a steam coil in A; the vapour is partially purified in the rectifier B; it is further freed from the less volatile components in the

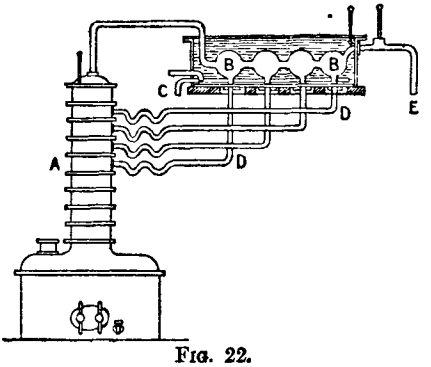


FIG. 22.

condensing apparatus C, and finally reaches the condenser D.

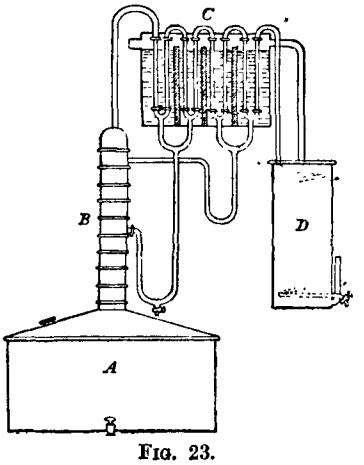


FIG. 23.

In Savalle's apparatus also the vapours pass first through a dephlegmator or analysing column, then through a surface or multitubular condenser, which is provided with a water supply, so regulated that its temperature is about that of the boiling-point of the liquid required; the liquid condensed in the regulated-temperature still-head returns to the dephlegmator, and the purified vapour passes on to the cold condenser.

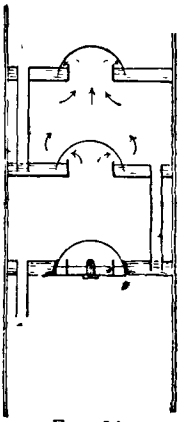


FIG. 24.

In most of the still-heads employed on the large scale, the vapour first passes through a dephlegmator, the construction of which varies considerably in different cases. Dubrunfaut's dephlegmator, employed in the French column apparatus, is shown in Fig. 24. Two others, devised by Savalle, are represented in Figs. 25 and 26.

In the Egrot dephlegmator an arrangement somewhat similar to the dome (Fig. 24) is used, but a large number of these domes are

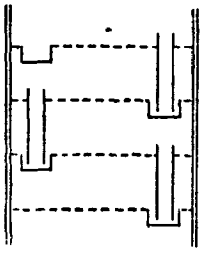


FIG. 25.

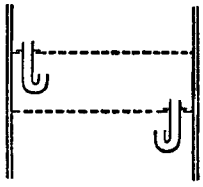


FIG. 26.

placed in each tray, and the condensed liquid is made to follow a zigzag course from the circumference to the centre of each tray.

The principle of the still-head in the Pistorius still is quite different. The vapour, entering a section (Fig. 27) of the still-head, is deflected from centre to circumference by the flat dome; it then passes back to the centre above the dome, and is partially condensed by the water in the shallow vessel above.

A simple and efficient still-head has been described by Foucar (Eng. Pat. 19999 of 1908). The column consists essentially of a helical septum which traverses the annular space between two concentric cylinders. The vapour

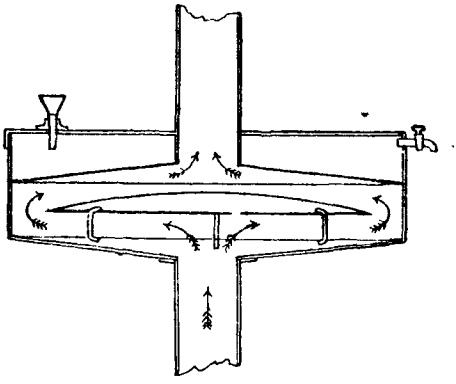


FIG. 27.

from the still passes up the long spiral passage before reaching the condenser. The inner cylinder can, if desired, be used as a thermostat, the column then acting as a regulated-temperature still-head.

A. Hirsch (J. Ind. Eng. Chem. 1910, 2, 409)

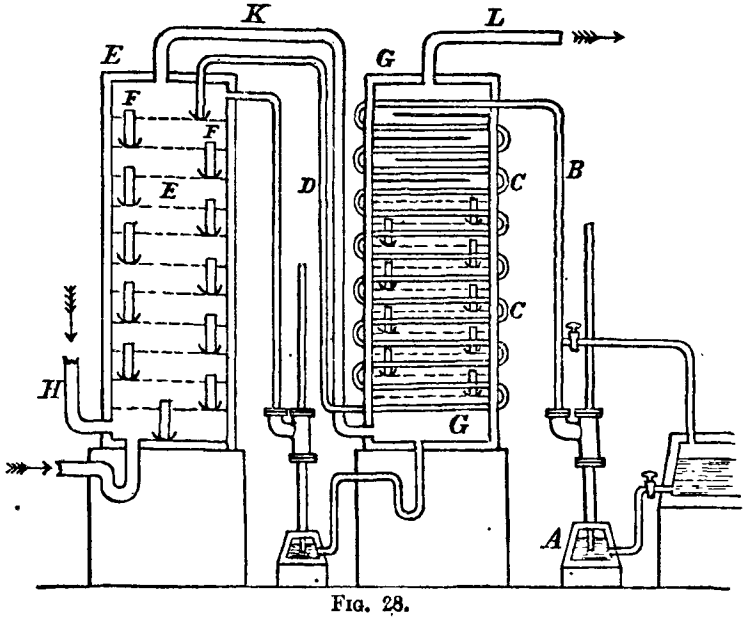


FIG. 28.

recommends the use of a differential condenser in the still-head, in the form of a spiral of metal tubing, through which a current of water of regulated initial and final temperature is caused to flow. The apparatus works easily and well so long as the temperature of the vapour leaving the still-head is considerably lower than that of the vapour entering it; but the difficulty of regulation increases greatly as this temperature-difference diminishes.

For work on the large scale Hirsch recommends the introduction of a differential condenser between the lower and upper parts of a rectifying column.

In England, the Coffey still is largely used; it differs considerably from those described, inasmuch as there is no large boiler, and the heat is supplied, not from an outer fire or steam-jacket, but by the condensation of steam in the wort; moreover, the process is continuous. The essential parts of the apparatus are shown in Fig. 28. The wort is pumped from a reservoir, A,

up the pipe B, and passes down the zigzag pipe CC, where it is heated by the ascending vapours, then up the pipe D, from which it is discharged into the column E. It is prevented from falling through the perforated plates of the column or analyser by the ascending vapours, but falls through the pipes F, F, from one plate to another until it reaches the bottom, when it is allowed to escape. Meanwhile, steam is passed into the analyser E by the pipe H, and causes the wort to boil, so that by the time it has reached the bottom it is completely deprived of alcohol. The ascending vapours force their way through the perforated plates of the analyser, a portion of the aqueous vapour being condensed by each washing, and the descending wort being thereby heated. On reaching the top of the column, the concentrated alcoholic vapour passes down the pipe K into the rectifier, and there ascends through similar perforated plates; but in the rectifier it is not washed by wort, but by the weak alcohol formed by the previous condensation of vapour. This dilute alcohol, on reaching the bottom of the rectifier, flows off into a reservoir, from which it is pumped into the top of the anslyser, where it mixes with the descending wort. In the upper part of the rectifier there are simply shelves, which compel the vapour to take the same zigzag course as the pipe which conveys the wort downwards. The purified and concentrated vapour then passes through the pipe L to the condenser. S. Y.

DISTYRENE $C_{16}H_{16}$. Produced by heating styrene (*q.v.*) with hydrochloric acid at 170° (Erlenmeyer, Annalen, 135, 122). Also, together with distyrenic acid and carbon dioxide, by prolonged boiling of cinnamic acid with diluted sulphuric acid (Fittig, Ber. 12, 1739–1744; Erdmann, Annalen, 216, 179–199).

A colourless optically inactive oil, with a blue fluorescence, which gradually disappears; sp.gr. 1·016 at 15°; b.p. 311°. On prolonged boiling yields toluene, *iso*propylbenzene, and some styrene; whereas *meta*styrene, produced from styrene on keeping, or heating in sealed tubes at 200° (Kovalevsky, Annalen, 120, 66), or with aqueous sodium bisulphite at 110° (Miller, *ibid.* 189, 341), passes almost quantitatively into styrene at 320° (Stobbe and Posjnak, *ibid.* 371, 259–286).

Distyrene yields benzoic acid on oxidation with chromic acid; and a crystalline dibromide $C_{16}H_{16}Br_2$ (m.p. 102°) on brominating in carbon disulphide solution.

According to Stobbe and Posjnak (Annalen, 371, 287–302), distyrene is $\alpha\gamma$-diphenyl-Δ^{α}-butene

$$C_6H_5{-}CH = CH{-}CH(CH_3){-}C_6H_5.$$

Distyrene disulphonic acid (dicinnamene disulphonic acid) $C_{16}H_{14}(SO_3H)_2$, described by Lange as obtained on heating γ-truxillic acid with sulphuric acid (Ber. 27, 1410–1415), is therefore not a derivative of distyrene.

Solid distyrene; m.p. 124°; obtained by distilling cinnamic acid or its calcium salt (Engler and Leist, Ber. 6, 256; Miller, Annalen, 189, 340), and by passing $C_6H_5{\cdot}C_2H_3Br_2$ over red-hot lime (Radziszewski, Ber. 6, 494), has been shown by Erlenmeyer (Annalen, 372, 249–251) to be stilbene.

DITA BARK. *Satween* (Ph. J. Trans. [3] 7, 110). The bark of *Alstonia scholaris* (R. Br.), an apocynaceous tree found in India, the Philippines, Eastern Australia, and tropical Africa (Ber. 11, 2234).

According to Harnack (*ibid.* 11, 2004; Chem Soc. Trans. [2] 36, 332), it contains only one base, *ditaïne*, a basic glucoside, having the composition $C_{22}H_{30}N_2O_4$; but Hesse (Annalen, 203, 144; Ber. 13, 1750; Pharm. J. [3] 11, 251, 331) found in it three bodies *ditamine*, $C_{16}H_{19}NO_2$; *echitamine* (echitammonium hydroxide), $C_{22}H_{28}N_2O_4,H_2O$, melting with decomposition at 106° (this base is identical with Harnack's *ditaïne*) and *echitenine* $C_{20}H_{27}NO_4$, a brown amorphous mass, melting above 120°, soluble in chloroform, alcohol, and ether. It dissolves in nitric acid with the production of a purple-red colour which quickly passes through green into yellow.

The milky juice of this tree has the same properties as guttapercha; when inspissated it softens in boiling water, is soluble in turpentine and chloroform, and receives and retains impressions. A decoction of the bark is used as an astringent tonic.

DITAÏNE *v.* DITA BARK.

DITTANY. The root of *Dictamnus albus* (Linn.) (ord. *Rutaceæ*), which is a native of the south of Europe. It contains a volatile oil, and also resin, bitter extractive matter, and gum; and was formerly employed in medicine, especially for the treatment of epilepsy (Aldis, Lond. Med. Gaz. 19, 142).

'*Cretan Ditany*' is the common name for *Origanum dictamnus* (Linn.), a native of the Levant.

DIURETIN. A compound of sodium theobromine and sodium salicylate (*v.* SYNTHETIC DRUGS).

DIVI-DIVI. Divi-divi consists of the dried pods of the *Cæsalpinia coriariæ* (Willd.), a tree 20–30 feet high, found in the West Indies and Central America. The pods are about 3 inches long and $\frac{3}{4}$ inch broad, are very thin, and frequently resemble in shape the letter S. From 40 to 45 p.c. of tannin is present, which consists of ellagitannin and probably also gallotannin. Extracts of this material have a somewhat unfortunate tendency to ferment, with simultaneous development of a deep-red colouring matter; but this can be prevented to some extent by the use of antiseptics. Divi-divi is largely imported for the preparation of leather, and is also employed for black dyeing, but its use is far more limited in this latter respect than myrabolans. A. G. P.

DOCIMACY or **DOCIMASY.** (*Docimasie*, Fr.) Originally the act or art of examining by test (*δοκιμασία*, a test), applied in metallurgy to experiments made to determine the nature and purity of a metal; in pharmacy, to the testing of medicines and poisons; in medical jurisprudence, to the different proofs to which the lungs of a new-born child are subjected, for the purpose of ascertaining whether it was born alive or dead (Dunglison). Uusually employed in chemistry as synonymous with assaying.

***n*-DODECANEDICARBOXYLIC ACID**

$$CO_2H(CH_2)_{12}CO_2H.$$

Prepared by hydrolysing the diethyl ester obtained by the electrolysis of an aqueous solution of the monoethyl ester of suberic acid

Brown and Walker, Annalen, 261, 123); or by the oxidation of chaulmoogric acid, obtained from chaulmoogra seeds (Barrowcliffe and Power, Chem. Soc. Trans. 1907, 568); m.p. 123°.

DODECATOIC ACIDS $C_{12}H_{24}O_2$.

1. *Lauric acid*, found by Marsson in laurel fat, a glyceride obtained from *Laurus nobilis* (Linn.) (Marsson, Annalen, 41, 330); also present in cocoa-nut oil (Görgey, *ibid.* 66, 295), in pichurin beans, in Dika bread, and in the fruit of *Cylicodaphne sebifera* (Oudemans, Zeitsch. Chem. 1867, 256); m.p. 43·5; sp.gr. 0·883/20° and 0·875/43·6°; b.p. 225·5° (100 mm.).

2. *Hordeic acid* is found among the products of the distillation of dried barley with dilute sulphuric acid; forms crystalline plates; m.p. 60° (Beckmann, J. 1855, 513).

DOG-TOOTH SPAR. The scalenohedral form of calcspar (*v.* CALCITE or CALCSPAR).

DOLOMITE. A native carbonate of calcium and magnesium, named after D. G. Dolomieu (1750–1801), a French geologist. The mineral, in its typical form, contains equal molecules of the two carbonates, corresponding to 54·34 p.c. of $CaCO_3$ and 45·66 p.c. of $MgCO_3$. This variety is sometimes termed *normal* dolomite. Rammelsberg recognises two other varieties, occurring less frequently than the normal type, and containing respectively $3CaCO_3,2MgCO_3$ and $2CaCO_3,MgCO_3$. But as the two carbonates are isomorphous, they occur associated in very variable proportions, and many of the massive dolomites are merely limestones more or less magnesian.

Dolomite crystallises in the rhombohedral system, and, unlike calcite, it commonly assumes the primitive rhombohedron (106° 15′); the forms are remarkable for presenting curved faces, while lenticular and saddle-shaped crystals are not unusual. Further, the degree of symmetry is not the same; etched figures and the occurrence of certain rare faces show that the crystals are rhombohedral with parallel-faced hemihedrism (the crystal class being the same as for dioptase and phenacite). Dolomite is slightly harder and denser than calcite; its H. being 3·5–4·5, and its sp.gr. 2·85–2·95. This sp.gr. is slightly higher than that calculated on the assumption of an isomorphous mixture of calcite and magnesite. This difference, together with the difference in the type of symmetry, indicates that normal dolomite is a double salt; and that crystals containing other proportions of calcium and magnesium carbonates must consist of isomorphous mixtures of dolomite with calcite or magnesite, or of the two latter alone.

The lustre of dolomite is often nacreous, especially in those varieties which contain a small proportion of $FeCO_3$, whence they are known as *pearl spar*. If the proportion of $FeCO_3$ increases, the mineral assumes, on weathering, a brownish tint, and is sometimes termed *brown spar*. $MnCO_3$ is often present to a slight extent, and imparts a faint pink tinge. Most varieties of dolomite show little or no effervescence with cold hydrochloric acid, but when powdered readily dissolve in the warm acid. Dolomite is soluble in water containing carbonic acid. The analyses of some of the dolomite springs in the Franconian Jura, by Gorup-Besanez, lead to the conclusion that natural waters acting on a normal dolomite may dissolve it, and redeposit the mineral without decomposition. According to Bischof's experiments, the action of carbonated water on an imperfect dolomite or *dolomitic* limestone, is to dissolve out the $CaCO_3$, the rock becoming relatively richer in $MgCO_3$ until a true dolomite is left; such a result, however, was not obtained by Gorup-Besanez (Annalen, 8, Suppl. 1871, 230).

Some of the finest crystals of dolomite occur at Traversella in Piedmont; while in this country the best examples are obtained from the Laxey Mine in the Isle of Man, from Derbyshire, Alston Moor, and Leadhills in Lanarkshire. A variety of asparagus-green colour, from Miemo in Tuscany, is termed *miemite*; it contains, according to Rammelsberg, 57·91 p.c. of $CaCO_3$; 38·97 of $MgCO_3$; 1·74 of $FeCO_3$; and 0·57 of $MnCO_3$. A compact snow-white variety from Gurhof in Lower Austria, has been distinguished as *gurhofite*.

Dolomite occurs not only as a mineral, but as a rock. Crypto-crystalline, granular, and compact varieties form mountain-masses of great magnitude, especially in the Eastern Alps, where they are largely developed in the Triassic series, and form the characteristic jagged-peaked mountains known as 'the Dolomites.' Sterry Hunt has shown that a large proportion of the Canadian limestones should be classed as dolomites, and even where the rock is a normal limestone it is commonly veined with dolomite, while the fossils also are more or less magnesian; this is notably the case with the Trenton limestone of Ottawa, belonging to the Lower Silurian formation.

In this country magnesian limestone is developed on a large scale, especially in the Permian series, corresponding with the *Zechstein*, or Upper Dyas, of German geologists.

The outcrop of the magnesian limestone stretches from the mouth of the Tyne, through Durham and eastern Yorkshire, to the plain of the Trent near Nottingham. Certain beds near Sunderland are remarkable for presenting concretionary varieties, which assume globular and botryoidal forms, with a radiating structure, varying in size from a marble to a cannon-ball; while near Marsden there occurs a laminated variety, notable for yielding thin slabs which display flexibility. The massive and granular varieties have been largely quarried for ages as a building stone, the principal quarries being near Anston in Yorkshire, Bolsover in Derbyshire, and Mansfield Woodhouse in Nottinghamshire. The best stone is of a warm creamy tint, easily worked, and, when well selected, extremely durable, the most durable kind being that which presents a crystalline texture and contains the two carbonates in molecular proportions, so as to form a normal dolomite. Southwell Cathedral, York Minster, and Ripon Cathedral offer good examples of the use of this stone; and the perfection with which the Norman carving at Southwell had been preserved led to the selection of Bolsover dolomite as the stone for the new Houses of Parliament. According to Daniell, who analysed the Bolsover stone for the Commissioners appointed to make the selection, it contains 51·1 p.c. of $CaCO_3$, 40·2 of $MgCO_3$, 1·8 of Fe_2O_3 and Al_2O_3, 3·6 of SiO_2,

and 3·3 of H_2O, &c. While this stone is, under ordinary circumstances, very durable, so large a quantity was required for the Houses that much of it was of inferior quality, and this has not proved satisfactory; other localities than those originally selected were laid under contribution, and stone was thus introduced which has yielded to the disintegrating influences of a London atmosphere.

A rock known as *dolomitic conglomerate* occurs in the South-West of England and in South Wales, and appears to be an old beach deposit of Keuper age. It consists chiefly of pebbles and angular fragments of carboniferous limestone, united by a cement more or less magnesian, and coloured with oxide of iron. The rock is quarried for burning, is used locally as a building stone, and, when polished, forms a handsome marble.

If magnesian limestone be calcined below a red heat, the carbonate of magnesium suffers decomposition, while the calcium carbonate is but slightly affected. On slaking the product, the caustic magnesia forms a definite hydrate, which is said to unite with the unaltered carbonate of calcium to produce a cement that offers considerable resistance to the action of water. Magnesian limestone, if argillaceous, though only to a small extent, has the reputation of forming good hydraulic cement; but some authorities allege that after a time the magnesian cements suffer alteration whereby their durability is greatly impaired. If dolomite be perfectly calcined, the product may be used for taking casts, since it 'sets' with water, like gypsum, though but very slowly.

Calcined dolomite is extensively employed as a lining for the converters used in the basic method of steel manufacture invented by Thomas and Gilchrist. The calcination is effected in either cupolas or regenerative kilns. After 9 hours' burning, the stone, though still hard, is found to have lost about half its volume and half its weight. This 'shrunk dolomite' is crushed, mixed with gas tar as a vehicle, and moulded into bricks, which are then heated until the tar is burnt off, when they are ready for use in the converter.

Dolomite treated with sulphuric acid yields the sulphates of calcium and magnesium, the two salts being readily separated by the greater solubility of the latter; hence magnesian limestone has been largely employed as a source of Epsom salts.

The origin of dolomite has given rise to much discussion, and probably more than one natural mode of formation must be recognised. While the frequent occurrence of dolomite with rock-salt and gypsum, and the paucity of associated fossils, suggest that it has been formed in inland waters, there are difficulties in the way of admitting its formation by direct precipitation. Sterry Hunt suggests that Na_2CO_3, resulting from the decomposition of soda-bearing minerals, like certain felspars, might be carried by fresh waters to the sea, and, on meeting with $CaCl_2$ and $MgCl_2$, decomposition would ensue, with formation of NaCl and $CaCO_3$ and $MgCO_3$. To account for the association of dolomite with gypsum, he assumes a reaction between $CaCO_3$ and $MgSO_4$, whereby $CaSO_4$ and $MgCO_3$ would be formed, and the latter might associate itself with fresh $CaCO_3$ to form the double carbonate. Most dolomite seems, however, to have been formed by the alteration of limestone. Water holding carbonate of magnesium in solution may cause the dolomitisation of a limestone through which it happens to percolate. The replacement of a molecule of $CaCO_3$ by one of $MgCO_3$, so as to form a dolomite, is accompanied by a diminution of volume to the extent of 12 or 13 p.c.; and it is characteristic of many dolomites to possess a cavernous structure. Elie de Beaumont suggested that this is due to the shrinkage consequent on dolomitisation; while von Morlot found by direct observation that the cavities in such a rock amounted to 12·9 p.c. of its bulk. It must be remembered that most limestones of organic origin, such as coral limestones, are more or less magnesian, and Richthofen and others hold that many of the Tyrolese dolomites are altered coral-reefs. It was formerly supposed that the dolomites of Tyrol were limestones which had been metamorphosed by heated magnesian vapour emitted from eruptive rocks; and Durocher found that by heating fragments of limestone with $MgCl_2$ they became partially dolomitised. It is much more probable, however, that the alteration has been effected by the magnesium salts in sea-water. (*v.* J. W. Judd and C. G. Cullis, The Atoll of Funafuti (Roy. Soc. London, 1904); E. W. Skeats, Quart. J. Geol. Soc. 1905, 61, 97; E. Philippi, Jahrb. Min. 1907, Festband, 297; G. Linck, Zts. Deutsch. Geol. Ges., 1909, 61, 230; *v.* CALCIUM and MAGNESIUM.) F. W. R.

DOMEYKITE. A copper arsenide Cu_3As, corresponding to copper 71·7 and arsenic 28·3 p.c. It occurs in reniform, botryoidal, and compact masses, of white or grey colour, with metallic lustre, rapidly tarnishing. H. = 3–3·5; sp.gr. 7–7·5. Readily fusible before the blowpipe, with emission of arsenical vapours. Soluble in nitric acid, but not in hydrochloric acid. It is found at Coquimbo and Copiapo in Chile, at Cerro las Paracatas in Mexico, and at Zwickau in Saxony.

Several other arsenides of copper, more or less like domeykite, are known. The *Algodonite* of F. Field is Cu_6As, and occurs at the Algodones Mine, near Coquimbo. *Whitneyite*, from Houghton Co., Michigan, U.S., described by F. A. Genth, is Cu_9As; and D. Forbes's *Darwinite*, named after Charles Darwin, is a similar mineral from near Copiapo. *Condurrite*, from Condurrow Mine, Cornwall, appears to be a mixture of arsenide of copper with various oxidised products derived from the alteration of tennanite or some kindred species. The names *Keweenawite*, *Mohawkite*, and *Ledouxite* have recently been applied to various copper arsenides from Michigan, in which the copper is in part replaced by nickel and cobalt. L. J. S.

DORMIOL *v.* SYNTHETIC DRUGS.

DOSS. Japanese name for a dyewood from an evergreen tree *Ilex Mertensii* (Maxim.), found in the Ogasawara and Okinawa Islands. Contains a dyestuff, *dossetin* $C_{15}H_9O_5$, crystallising in yellow needles; m.p. 271°–272° (Ito, J. Soc. Chem. Ind. 1908, 440).

DOUBLE SCARLET, BRILLIANT SCARLET *v.* AZO- COLOURING MATTERS.

DRAGON'S BLOOD. A resin used as a red pigment (*v.* PIGMENTS; also RESINS).

DRIERS (in the United States also termed 'Japans') is the trade term for those metallic oxides, chiefly oxides of lead and manganese (litharge, red lead, manganese dioxide) or their inorganic salts, which were formerly used exclusively in the process of oil boiling as 'driers.' More recently acetate, oxalate, and borate of manganese have been employed. Since metallic salts of rosin acid have the same property, such salts are also manufactured as 'driers.' They are obtained either by precipitating rosin soap solutions with solutions of metallic salts, or by fusing together a metallic oxide with colophony. Hence these are distinguished in commerce as 'precipitated' driers, and 'fused' driers. The latter are readily discriminated from the former by their not containing any moisture. Metallic salts of linseed oil fatty acids are now used as driers; they can be prepared either by precipitation or by the dry process, hence both 'precipitated' manganese linoleate, 'precipitated' lead linoleate, and 'fused' manganese linoleate, &c., are obtainable. The driers prepared from linseed oil fatty acids, as also from rosin (colophony), are soluble in oil of turpentine, ether, chloroform, and linseed oil itself. Hence they are also termed in commerce 'soluble driers.' Solutions of these driers in linseed oil or in turpentine oil, or in a mixture of both, are obtainable in commerce under the name 'liquid driers,' 'terebene,' and other fancy names.

The function of these driers appears to be to absorb oxygen from the air and transfer it on to the linseed oil, thus accelerating its drying to a flexible film when exposed to the air. On this assumption, the fact that litharge and manganese dioxide act as driers will be best explained by stating that at the high temperature at which linseed oil is 'boiled,' the oxides saponify the linseed oil, forming therewith lead or manganese soaps, which then act in their turn in the manner indicated above. The following are the analytical data obtained by the author in the examination of a drier:—

	Per cent.
Ash	18·6
Fatty and rosin acids	83·4

The more detailed examination gave the following result:—

	Per cent.
Lead oxide	10·99
Manganous oxide	6·79
Iron peroxide	0·47
Calcium oxide	0·56
Rosin acids	38·32
Oxidised acids	4·24
Other fatty acids	40·86

It should, however, be understood that the results furnished by chemical analysis alone are not sufficient to supply the data on which to base an opinion as to the properties which a drier will impart to the oil. The colour and drying power of the boiled oil to be prepared and other conditions greatly influence the choice and the quantity of a drier to be employed on a large scale. J. L.

DROP GUM or **GAMBOGE** *v.* PIGMENTS.

DROSERA WHITTAKERI. The *Drosera Whittakeri* is to be found in Australia, and grows plentifully on the hills near Adelaide. This plant is provided with a tuber, which consists of an inner solid but soft nucleus full of reddish sap or juice, and an outer series of easily detached thin, and more or less dry, layers of an almost black material. Between these layers are to be found small quantities of a brilliant red colouring matter, the amount varying in tubers of different size and age, but apparently more plentiful in the older plants (Rennie, Chem. Soc. Trans. 1887, 51, 371; 1893, 63, 1083).

The colouring matter is extracted from the tubers by means of hot alcohol, the solution evaporated, and the residue, containing a little alcohol, is then mixed with some water and allowed to stand. The product is dried, sublimed, and the brilliant vermilion powder, which contains two substances, is fractionally crystallised from boiling alcohol or acetic acid.

The more sparingly soluble compound $C_{11}H_8O_5$, forms red plates, melting at 192°–193°, dissolves in alkaline solutions with a deep-red violet colour, and gives a *triacetyl derivative*, $C_{11}H_5O_5(C_2H_3O)_3$, m.p. 153°–154°.

The *monosodium* compound $C_{11}H_7O_5Na,2H_2O$ gives dark reddish-brown needles, the *disodium* compound, $C_{11}H_6O_5Na_2,H_2O$, brown needles, and the *calcium* compound $(C_{11}H_7O_5)_2Ca,3H_2O$, dark-brown crystals.

By treatment with stannous chloride or hydrochloric acid, this substance, $C_{11}H_8O_5$, yields a reduction product $C_{11}H_{10}O_5$, in yellow needles, m.p. 215°–217°. When dry, this is stable in air, but if left in contact with alcohol or water, it soon becomes red owing to oxidation. According to Rennie, it is probable that the original colouring matter is a *trihydroxymethylnaphthoquinone*, in which case the substance $C_{11}H_{10}O_5$ will consist of the corresponding hydroquinone derivative. The more readily soluble compound contained in the tubers possesses the formula $C_{11}H_8O_4$. It crystallises in red needles, m.p. 174°–175°; dissolves in alkaline solutions with a deep-red colouration; and gives a *diacetyl* derivative $C_{11}H_6O_4(C_2H_3O)_2$, in yellow needles, m.p. 107°–110°. A. G. P.

DRUMINE. An alkaloid stated to be present in *Euphorbia Drummondii* (Ogston, Brit. Med. Jour. 1887, 451).

DRY CLEANING. French or chemical cleaning, *Nettoyage à Sec.* A process of removing dirt, grease, &c., from fabrics by solvents other than water, such as petroleum benzine, coal-tar benzene, carbon tetrachloride, &c. The substitution of such liquids for water seems to have been first made in France during the middle of the last century by the application of 'camphene,' a terpene used at that period for illuminating purposes.

The process was introduced into the United Kingdom, in 1866, by Messrs. Pullar & Sons, who greatly developed it, employing machinery to a large extent in place of the hand labour formerly used.

The solvents mainly used at the present time are 'benzines,' usually obtained from American and Borneo petroleum, of sp.gr. 0·78; boiling between 80° and 120°. The benzols employed are what are known commercially as 90's and 50's. They may contain sensible quantities of carbon disulphide, thiophen, and possibly other sulphur products, which are apt to impart a disagreeable smell to the fabric. Carbon

tetrachloride, on account of its relatively high price, is only used to a limited extent. It has the great advantage over the hydrocarbons that it is uninflammable, and can be employed in particular cases where the use either of benzine or of benzol is inadmissible. (For a method of valuing benzine for the purpose of the dry cleaner, *v.* Trotman, J. Soc. Chem. Ind. 1906.)

Thiophen in benzol may be detected by the isatin and sulphuric acid reaction (*v.* THIOPHEN). (*Cf.* Schwalbe, Chem. Zeit. 1905.)

Carbon disulphide may be detected by the formation of a precipitate with phenylhydrazine, and determined quantitatively by conversion into potassium xanthate by means of alcoholic potash (*v.* CARBON DISULPHIDE).

An admixture of paraffin hydrocarbons with the benzol may be recognised by nitrating the sample with nitrosulphuric acid and subsequent steam distillation.

The carbon tetrachloride employed for degreasing should be free from hydrochloric acid or traces of free chlorine. It should also contain no chloroform or phosgene gas, which are apt to act deleteriously upon the workpeople.

Special soaps, soluble in benzine, are employed in dry cleaning. They not only assist the degreasing, but diminish the risk of fire. The soaps consist of practically anhydrous oleates or stearates of potash or soda made by melting together oleic acid and soap, or by dissolving the alkali in methylated spirit, and adding to the solution the requisite quantity of oleic acid or melted stearic acid. Strong ammonia solution may be employed instead of potash or soda.

(For a description of the methods and machinery employed in modern processes of dry cleaning, and of the apparatus for the recovery and purification of the solvents used, *v.* Dyeing and Cleaning, by F. J. Farrell, Griffin & Co., Ltd. 1910.)

DULCAMARA. *Bittersweet, Woody nightshade.* (*Douce amère*, Fr.; *Bittersüss*, Ger.) The young branches of the *Solanum dulcamara* (Linn.), a climbing plant with purple flowers and red berries inhabiting the British Islands and most parts of Europe (Woodville, Med. Bot. 33; Bentl. a. Trim. 190). The drug appears to be going out of use, but in the form of decoction it is sometimes administered as a remedy in rheumatism and certain skin diseases.

The investigations of Pfaff (Mat. Med. 6, 506), Desfosses (J. Pharm. Chim. 6, 414), Pelletier (*ibid.* 6, 416), and others went to show that bittersweet contained a glucoside 'dulcamarin,' 'picroglycion,' or 'dulcarin,' and also a compound believed to be the alkaloid 'solanine' (*cf.* Meissonier, Annalen, 1, 368). Continuing an inquiry of Wittstein's (Vierteljahrs. pr. Pharm. 1, 364, 495), Geissler has shown (Arch. Pharm. [3] 6, 1010) that dulcamara contains a definite compound, *dulcamarin* $C_{22}H_{34}O_{10}$, together with a substance resembling solanine, which, however, does not yield sugar when heated with dilute acids. The dulcamarin of Geissler is a slightly yellow, inodorous, amorphous powder having a strong bitter taste followed by sweetness. It is soluble in water and alcohol, but insoluble in ether, chloroform, and benzene. It forms a lead salt $C_{22}H_{32}PbO_{10},5H_2O$. With dilute sulphuric acid it breaks down into *glucose* and *dulcamaretin* $C_{16}H_{26}O_6$; thus

$$C_{22}H_{34}O_{10}+2H_2O = C_{16}H_{26}O_6+C_6H_{12}O_6.$$

Dulcamaretin is resinous, and forms the lead salt $C_{16}H_{24}PbO_6$.

An examination of *Solanum dulcamara* by Davis (Pharm. J. [iv.] 15, 160) has revealed, in addition to dulcamarin, the presence of *solanine* $C_{43}H_{75}O_{12}N$, m.p. 235°; *solanidine* $C_{41}H_{71}O_2N$, m.p. 205°; and *solanein*

$$C_{48}H_{75}O_{13}N.$$ A. S.

DULCITOL *v.* CARBOHYDRATES.

DUMASIN *v.* KETONES.

DUNGING-SALT. *Sodium arsenate* (*v.* ARSENIC).

DUOTAL *v.* SYNTHETIC DRUGS.

DU PONT POWDER *v.* EXPLOSIVES.

DURENE *v.* CYMENES.

DURENOL *v.* PHENOL AND ITS HOMOLOGUES.

DUTCH PINK or **ITALIAN PINK** *v.* PIGMENTS.

DUTCH ULTRAMARINE. *Cobalt blue* (*v.* COBALT and PIGMENTS).

DYEING. The art of dyeing consists in imparting colour to the substance of various materials, usually textile fabrics, in such a manner that it is not readily removed or altered by those influences to which the dyed material is subsequently exposed. *Tinting* is essentially the same as dyeing, but the term is applied to the production of light shades only. In *staining*, the colour is not so permanently fixed as in dyeing, but in all these processes the colouring substance is presented to the material in a dissolved condition. In textile *printing*, the colour is applied to portions of the material only, thus producing a pattern, but in other respects, many printing operations are, as regards principle, similar to dyeing. In *painting*, on the other hand, a more or less opaque pigment is applied to the material by means of adhesives, thus partially or entirely obscuring the true surface.

Dyeing is of chief importance in connection with the textile industries, but many other materials are coloured by dyeing processes, such, for example, as leather, feathers, horn, ivory, bone, straw, and wood.

The various materials above enumerated show remarkable differences in behaviour towards any particular dyestuff. Wool, silk, leather, feathers, horn, and animal skin products in general, behave somewhat similarly towards colouring matters, but the dyeing properties of cotton, linen, and other vegetable products are quite different.

Differences quite as marked are to be noted in the behaviour of various colouring matters towards one and the same material, and thus, in dyeing operations, the nature both of the material to be dyed and of the colouring matter employed, have to be taken into account.

The theory of dyeing. The precise cause or causes of the different behaviour of the textile fibres in dyeing is still a matter of acute discussion; but there is little doubt that the chemical nature and physical condition of the fibre and of the dyestuff all play their part in the complicated phenomena of dyeing.

The earliest theory with regard to the

fixation of dyes was that the action is purely mechanical, and it is still urged by many that rarely in dyeing processes is there direct evidence of chemical combination between fibre and dyestuff. Both bodies, as a rule, retain their individual chemical and physical properties unchanged, and the dye can frequently be removed from a fibre by means of alcohol or other solvent.

In its earliest form, the mechanical theory was put forward by Hellot and d'Apligny in 1780. (The Art of Dyeing Wool, Silk, and Cotton, being a translation of Hellot's L'Art de la Téinture des Laines (1734); and d'Apligny's *L'Art* de la Teinture des fils de Coton (1776).) They assumed that the particles of colouring matter became embedded in the minute pores permeating the fibre substance. Crum (Chem. Soc. Trans. 16, 404) strongly supported this theory, while Müller-Jacobs (J. Soc. Dyers, 1885, 63) expressed much the same idea in attributing the fixation of dyes to membranous diffusion. It has, however, been shown by several investigators that dyeing processes do not obey the general laws of osmosis. v. Georgievics (J. Soc. Chem. Ind. 1895, 149) considers dyeing is chiefly due to surface attraction. Witt (Färber-Zeit. 1890) put forward a modification of the mechanical theory. He regards the fibres as solid solvents in which the dyestuff dissolves, the latter being withdrawn from its aqueous solution in the same way as, *e.g.*, ether will extract many substances from their aqueous solution. The degree to which a dye-bath can be exhausted will then depend upon the relative solubility of the dyestuff in the acid or neutral dye liquor and in the fibre substance at the temperature used. Krafft (Ber. 1899, 1608) attributes dyeing phenomena to a separation of the dyestuff upon the fibre in a colloidal state, and this view has been supported by Biltz (*ibid.* 1904, 1766), Linder and Picton (Chem. Soc. Trans. 1905, 1931), and Dreaper (J. Soc. Chem. Ind. 1905, 223).

The chemical theory of dyeing was originally put forward by Macquer and Bergman in opposition to the mechanical theory of Hellot and d'Apligny, and has received much experimental support from Persoz, Berthollet, Chevreul, Kühlmann, Vignon, Knecht, and many others. It is mainly based on the following facts: wool and silk fibres contain amino-acids, and thus possess strongly marked acidic and basic functions. Cellulose, the essential constituent of the vegetable fibres, is chemically much less active, and dyes much less readily than wool and silk, but under certain conditions it exhibits weakly acidic functions. All dyestuffs (with few exceptions) possess either acidic or basic properties, or are in the form of salts, which dissociate in the dye-bath; and chemical combination between fibre and dyestuff would thus, *primâ facie*, be expected. Moreover, *lanuginic* and *sericinic acids*, which are produced respectively by the hydrolysis of wool and silk, precipitate both acid and basic dyes from their aqueous solution (Knecht and Appleyard, J. Soc. Dyers, 1889, 72).

A full discussion of the evidence for and against the mechanical and chemical theories of dyeing cannot be here entered upon, but a general review indicates that the attempt to cover all dyeing phenomena by any one simple explanation must fail, and that many factors are concerned, the relative importance of which varies in different cases. In the dyeing of wool or silk, with acid or basic dyes, it may be taken as established that chemical combination occurs, but prior to this some hydrolysis of the fibre, and more or less complete ionisation of the dyestuff takes place. Surface concentration of the dye on the fibre probably also occurs, and the coagulation and precipitation of the dissociated colloidal dyestuff may also play a part. This is rendered more probable by the recent observation that the temperature of maximum *absorption* of dye does not (in the cases investigated) correspond with that of maximum *fixation* (Dreaper, Trans. Faraday Soc. 1910, pt. i. Haldane-Gee and Harrison, *ibid.*); the former possibly coinciding with the point of maximum coagulation and precipitation, and the latter indicating the point of maximum degree of chemical combination. Whether the superficially precipitated dye penetrates the fibre by osmosis or by 'solid solution' is mainly a question of definition of terms.

In the case of the dyeing of vegetable fibres, the same factors probably operate, but their relative importance is not the same, the physical factors—precipitation, surface attraction, and osmosis—predominating over the effect of direct chemical action.

Classification of colouring matters. It has already been pointed out that dyestuffs vary in their behaviour. If, *e.g.*, separate pieces of wool are boiled in solutions of (*a*) logwood, (*b*) indigo, (*c*) magenta, and (*d*) picric acid, the following results are obtained: (*a*) the wool acquires a brown stain; (*b*) the wool remains undyed, the indigo floating about in an insoluble condition; (*c*) the wool is dyed a magneta colour; and (*d*) the wool is dyed a full yellow. If the experiment is repeated on wool which has been previously mordanted with potassium dichromate, the result will be that in (*a*) the wool is dyed black, whereas in (*b*), (*c*), and (*d*), similar results are obtained as in the previous experiments. Logwood, therefore, must be applied in conjunction with potassium dichromate or some similar substance, *i.e.* with a mordant; whereas magenta and picric acid dye without such aid, and indigo requires a special process, the nature of which is not indicated by the results of the above-described experiments.

Colouring matters may be divided into three groups on the lines indicated above, viz.: (1) those which must be applied in conjunction with a mordant; (2) those which dye direct from their solutions; and (3) those requiring special processes.

This classification is practically identical with that of Bancroft (Philosophy of Permanent Colours, i. 118, London, 1794), who, upwards of a hundred years ago, divided colouring matters into *substantive dyes* and *adjective dyes*; the former class comprising those which dye directly from their solutions, and the latter being composed of those dyes which require mordants. Nietski (Färber-Zeit. 1889–90, 8) uses the terms *direct dyes* and *mordant dyes* in exactly the same sense, and both Bancroft's and Nietski's terms are still in use. Hummel (The Dyeing of Textile Fabrics, 1st ed. 1885, 147) also classifies dyestuffs into two groups: *monogenetic dyes* being such as are capable of producing one colour only, while *polygenetic dyes* produce distinct colours

with different mordants. The members of the first group are *coloured bodies*, and these merely require to be fixed upon the fibre, whereas the *colouring principles* comprising the second group only develop a colour when combined with a mordant.

It will be seen that these three systems of classification closely correspond, the terms *substantive dyes*, *direct dyes*, and *monogenetic dyes* being almost synonymous, as are *adjective dyes*, *mordant dyes*, and *polygenetic dyes*. It should, however, be pointed out that none of these classifications is absolute; magenta, for example, is a direct dye as applied to wool, but requires a mordant when used for cotton.

A distinct method of grouping dyestuffs is that of Benedikt (The Chemistry of the Coal-tar Colours, 1886, 29), who distinguishes between *colour acids*, *colour bases*, and *neutral colouring matters*. Both colour acids and colour bases are fixed on the fibre in the form of salts, but whereas in the colour acids the essential colour-producing group resides in the acid portion of the compound, in the colour bases the reverse is the case. Alizarin red, dyed on wool, is a salt of which alumina forms the basic and alizarin the acid constituent. Alizarin is therefore a *colour acid*. Similarly, the red pigment formed on dyeing tannin-mordanted cotton with magenta is a combination of rosaniline base with tannic acid. Magenta is therefore a *colour base*. Indigo and many other vat dyes are *neutral colouring matters*.

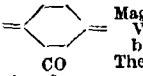
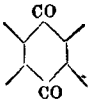
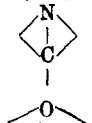
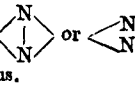
All the above schemes of classification are defective, both from the points of view of the practical dyer and the chemist. As regards practical application, the large number of dyestuffs now on the market may, however, be satisfactorily classified into the following groups: (1) *mordant dyes*; (2) *acid-mordant dyes*; (3) *acid dyes*; (4) *direct dyes*; (5) *basic dyes*; (6) *sulphide dyes*; (7) *vat dyes*; (8) *ingrain dyes*.

The classification of dyes according to chemical constitution is based upon the existence, in all members of each class, of a certain group of atoms, upon the integrity of which their colouring power depends. This is termed the *chromophorous group*, the theory being first put forward by O. N. Witt, in 1876. The introduction of such a chromophor into a suitable colourless compound is accompanied by the development of colour, *e.g. benzene* (C_6H_6) is colourless, but *azobenzene* ($C_6H_5{-}N{=}N{-}C_6H_5$) is orange-coloured. Many substances, however, such as azobenzene, although strongly coloured, are devoid of dyeing power. Such bodies are termed *chromogens*, and in order to convert them into useful dyes, the introduction of a salt-forming group is necessary; these groups, in this connection, being termed *auxochromous groups*. Thus, whilst *azobenzene* is not a dyestuff, both *amino-azobenzene* and *hydroxy-azobenzene* are useful dyes. In these compounds, the azo- group ($-N{=}N-$) is the *chromophor*, and the amino- or hydroxyl- group is the *auxochrome*.

The presence of both a chromophor and an auxochrome does not, however, necessarily indicate that a substance is a useful dye. For example, *trinitroaniline*, $C_6H_2(NO_2)_3NH_2$ contains the chromophor (NO_2) and the salt-forming auxochrome group (NH_2); but it is not a useful dyestuff, because the basic character of the auxochrome is neutralised by the strongly acidic chromophor. On the other hand, trinitrophenol $C_6H_2(NO_2)_3OH$, is the useful dyestuff picric acid.

Those dyestuffs which do not contain a salt-forming auxochrome cannot be applied by ordinary dyeing processes, and the fact that a special process is required, *e.g.* for indigo, is not primarily due to its insolubility, but to its neutral character.

The scheme of classification, based on the chromophor, distinguishes the following groups:—

Group	Chromophor	Typical dyes
1. *iso*-Nitroso- or oxime	$>C{=}O$ / $>C{-}N{\cdot}OH$	Resorcin green, dioxine, gambine.
2. Nitro-	$-NO_2$	Picric acid, napthol yellow.
3. Azo-	$-N{=}N-$	(*a*) *Basic*—chrysoidine, Bismarck brown, Janus red. (*b*) *Acid*—azo- oranges and scarlets, naphthol black, diamond black. (*c*) *Direct*—benzopurpurin, diamine colours, direct blacks.
4. Triphenyl-methane		Magenta, methyl violet, Victoria blue, patent blue, malachite green.
5. Oxyketone		The alizarin dyes.
6. Pyronine		Rhodamine, violamine, eosins.
7. Acridine		Acridine yellow, orange, and scarlet.
8. Oxazine		Meldola's blue, gallocyanin, Capri blue.
9. Thiazine		Methylene blue, thiocarmine.
10. Azines		Safranines and indulines.
11. Miscellaneous.		

This classification of dyestuffs into chemical groups is of importance in the identification and testing of dyestuffs, as the constitution of the compound determines its behaviour towards reagents. It is not, however, a convenient one as regards the practical application of the dyestuffs.

Essential properties of a dyestuff. In order to rank as a useful dye, a substance must possess certain essential features. A *direct dye* must not only possess a colour of considerable intensity and permanence, but must also be capable of easy fixation on textile fibres without injury to fibre or dyestuff. For example, both vermilion and azo-scarlet possess a brilliant colour, but the former is not a dyestuff, because it cannot be applied or produced by dyeing processes. A *mordant dye*, on the other hand, need not possess a strong colour, and may, in fact, be colourless. It must, however, be capable of producing strongly coloured and insoluble colour-lakes in combination with suitable mordants. *Vat dyes*—*e.g.* indigo—are, as a rule,

quite insoluble in water, and therefore cannot be applied by an ordinary process. The essential feature of this group is that their reduction products are soluble in alkaline solutions, and on this fact the method of application depends.

In order to constitute a dyestuff a body must, therefore, either be strongly coloured in itself or be capable of producing coloured lakes. It must also be of such a character that it can be fixed upon textile material from an aqueous solution, and it must produce a colour which possesses sufficient permanency and resistance to washing and other influences.

Operations preliminary to dyeing processes. In any dyeing operation, the chief bodies concerned are the fibre to be dyed and the dyestuff. In their natural condition, all textile fibres contain impurities which not only detract from their appearance, but prevent their being satisfactorily dyed. The removal of these impurities is the object of the washing, scouring, and bleaching processes which the crude fibres undergo.

A great bulk of manufactured textile material, chiefly cotton and linen, is used in the undyed condition, but wool and silk are usually dyed.

Dyeing processes. Dyeing may take place at various stages of the manufacture of textiles. '*Piece dyeing*' is generally employed when a plain-coloured material is required, being the most economical and convenient process. If a coloured pattern is required, the material must be dyed before weaving, and the process may then be carried out on the raw wool or cotton ('*wool dyeing*,' '*cotton dyeing*'), at an intermediate process ('*sliver*' or '*slubbing dyeing*') or upon the spun yarn '*yarn dyeing*,' '*hank dyeing*,' '*cop dyeing*,' '*warp dyeing*').

Wool is dyed in all these forms; silk, almost exclusively in the form of yarn; and cotton, chiefly as warps, cops, or pieces.

The dyeing of wool. Wool may be dyed with a greater range of colouring matters than any other textile fibre. All the various classes of colouring matters enumerated in the classification based on practical application (*see* p. 282) are used in the dyeing of wool; the most important groups being the *mordant*, the *acid-mordant*, the *acid* and the *direct* dyes, as well as the *vat dye*, indigo. In boiling solutions, the affinity of wool for dyestuffs is generally greater than that of silk, but at temperatures below 60° the relative affinity is frequently reversed. By a suitable selection of dyestuffs and control of the process, it is therefore possible to dye the wool and silk in a woven fabric to different shades, or to produce a uniform colour on the two fibres. As a general rule, dyeing processes which produce good results on wool are entirely unsuited for cotton, and it is an easy matter to dye one of the two fibres when present in a mixed fabric and leave the other practically unstained. If both fibres are to be dyed the same or different colours, two distinct processes are, as a rule, required.

Different varieties of wool behave differently in dyeing, the finer wools, such as merino, requiring a larger amount of dyestuff to produce a given shade than the coarser qualities, *e.g.* Lincoln wool. The absorption of dye is, however, by no means entirely governed by the diameter of the fibre, *e.g.* fine silky mohair is very difficult to dye, probably on account of the close texture of the external scales. Fibres taken from different portions of the same fleece also vary somewhat in dyeing properties; and wool taken from the skin of animals slaughtered for meat, or from diseased animals, also differs as regards its affinity for dyes. All these differences are shown to a much greater extent with some dyestuffs than with others.

The affinity of wool for certain dyestuffs may be increased by suitable treatment with acids, alkalis, or oxidising agents (bleaching powder or hydrogen peroxide solution), or may be diminished by a treatment with tannic acid solution and in other ways. Various colours may thus be produced by a '*piece-dyeing*' process by weaving together untreated wool and wool treated with one or other of the above-mentioned reagents.

The behaviour of wool towards solutions of metallic salts governs the use of these bodies as mordants. When boiled in solutions of salts which are neutral to litmus (*e.g.* sodium chloride), no change takes place; but when boiled in solutions of salts of the heavy metals having an acid character (*e.g.* sodium dichromate), a decomposition of the salt takes place, and an insoluble basic salt or a hydrated oxide is fixed upon the fibre.

The dyeing of silk. In general behaviour towards colouring matters, silk resembles wool, but, as a rule, dyes are fixed on silk in a less permanent manner than on wool. The dyeing of silk appears to depend, to a greater extent, on absorption, and to a less extent on chemical action. The *acid*, *basic*, and *direct* dyes are chiefly used on silk, but other classes, *e.g.* the *mordant* and *vat* dyes, are also employed, though they tend to detract somewhat from the brilliant lustre and suppleness on which the beauty of silk depends. The maximum absorption of dyes by silk usually takes place at 60°–80°, and not at 100° as in the case of wool.

The so-called '*dry dyeing*' process sometimes employed for silk consists in the use of benzene or other volatile liquid as a solvent for the colouring matter in place of water. The usual dyestuff-salts are not soluble in benzene, but the fatty acid compounds or resinates of basic dyes are readily soluble.

The mordanting of silk with metallic salts is usually carried out in cold concentrated solutions of basic salts, chiefly basic aluminium sulphate for colours, and basic ferric sulphate or ferrous acetate for blacks.

The production of black upon silk is a matter of great importance, and is almost a trade to itself. The silk is first immersed in a solution of chestnut extract or other tannin matter, and then in a solution of basic ferrous acetate (pyrolignite of iron) or ferric sulphate ('nitrate of iron'). By successive alternate treatments in these liquors, the silk may be weighted to the extent of 400 p.c. It is then dyed with logwood extract. There are a number of alternative processes for the black dyeing of silk.

Wild silks, of which *Tussur* is the chief variety, are much more difficult to dye than ordinary silk, the fine fibrillæ of which the fibre is composed being very impervious. The band-like flat surface of the fibre also reflects the light in such a manner that a white shiny

appearance may be produced instead of a rich, intense colour or black.

Artificial silks, consisting essentially of cellulose, are more allied to cotton than to silk as regards dyeing properties. Those varieties produced from collodion dye more readily with the basic dyes than do cotton or the artificial silks obtained from cuprammonium or zinc chloride solutions.

The dyeing of cotton. Cotton is dyed chiefly in the form of hanks or warps, less frequently as piece goods. The dyeing of cotton on the spool, cop or beam is, however, rapidly extending.

The dyeing properties of cotton differ greatly from those of wool, and therefore the processes and materials used also differ. Until the discovery of Congo red in 1884, there were three dyestuffs only, which were capable of dyeing cotton directly from their aqueous solution—*turmeric*, *safflower*, and *annatto*—but there are now a large number of synthetic substantive dyes by means of which any desired shade can be obtained. The very numerous class of *acid dyes* which are of such great importance in wool and silk dyeing are inapplicable to cotton.

Cotton has no affinity for metallic salts, and therefore does not become mordanted by boiling in their solutions. Indirect methods have therefore to be adopted in applying the basic mordants required for the fixation of the mordant dyestuffs on cotton. This fibre exhibits a remarkable affinity for tannic acid, which is withdrawn from dilute solution and concentrated on the fibre to a considerable extent. The tannic acid may then serve for the fixation either of metallic mordants or of basic dyestuffs upon the fibre.

The *vat dyes for cotton* are now assuming a very prominent position, since, by their use, extremely fast colours are obtained.

The so-called *ingrain dyes* are used almost exclusively on cotton. The term is applied to designate a class of dyes which are produced *in situ* on the fibre by precipitation.

Mercerised cotton is virtually a distinct textile fibre; and whilst its dyeing properties are essentially the same as those of ordinary cotton, its treatment requires special precautions on account of its great affinity for the direct dyes.

The dyeing of linen. The behaviour of linen towards the respective classes of dyestuffs is similar to that of cotton, but it is more difficult to dye. The inferior dyeing affinity of linen is probably due to the different physical structure of the fibre.

The dyeing of jute. Although a cellulose derivative, jute differs from cotton and linen, both in its chemical composition and properties. As regards dyeing processes, it behaves, to a certain extent, like tannin-mordanted cotton, and may be dyed not only with the ordinary *direct*, but with the *basic* colouring matters without the aid of a mordant.

The dyeing of leather. Leather resembles wool in dyeing properties, but the difficulty of dyeing it in fast colours is increased by the necessity of using lukewarm liquors only, since boiling water destroys ordinary leather. Certain of the newer methods of producing leather, *e.g.* chrome tannage yield a product which will withstand boiling solutions. It is very important as regards the permanence of the leather (when used *e.g.* for bookbinding or furniture covering) that no mineral acid should be employed in the dyeing process. As a substitute, formic acid may be recommended. The *acid* and *basic* colouring matters are chiefly employed, the *mordant* dyes being used to a less extent.

The dyeing of feathers. The chief cause of difficulty in the dyeing of feathers is their natural water-resisting property. This is due partially to their ultimate physical structure, and partially to the natural grease present, The midrib is specially difficult to dye. Apart from these special difficulties, feathers behave in dyeing, like wool, and may be dyed with *acid*, *basic*, *direct*, or *mordant* dyes. Reds, browns, blues, and other colours are usually dyed with acid dyes, but the most satisfactory blacks are obtained by successive and repeated treatments with logwood extract, and ferrous sulphate with potassium binoxalate. Dyeing must proceed for a considerable period at the boil, in order to ensure penetration.

The dyeing of horn. Horn is dyed in strong solutions of *acid* dyes by steeping for a long period in the cold or slightly warm baths, which are acidified with acetic or formic acid. Since it contains sulphur, horn may be dyed brown by steeping in a solution of sodium plumbite, which results in the formation of lead sulphide. Black is also produced by alternate steepings in solutions of mercuric nitrate and potassium sulphide.

The dyeing of ivory. Both *acid* and *basic* dyes may be employed in the dyeing of ivory, the former being used with addition of acetic or formic acid in hot solutions. Alcoholic solutions of colouring matters may also be employed. Red is frequently dyed by the cochineal single-bath process used for wool.

Black is produced either by the logwood and iron or aniline black process, as used in cotton dyeing, or by means of silver nitrate.

The dyeing of wood. The method of dyeing wood in bulk is to boil or steam it to remove the resins, and then treat it in an apparatus similar to that employed in creosoting. The wood is placed in a closed vessel which is exhausted by a vacuum pump, and when the air has been sucked out from the pores as completely as possible, the hot dye liquor is admitted into the vessel and put under pressure by a force pump. The direct and basic dyes may be employed. Wood is usually dyed black by alternate treatments with logwood extract and sodium bichromate solution.

The dyeing of straw. Straw is largely dyed for use in the manufacture of hats and baskets. There are two commercial varieties, distinguished as *chip* and *straw*. Chip is readily dyed by means of the *direct cotton dyes* or the *sulphide dyes*, and many *basic* and *acid dyes* in neutral solution may also be employed. The process must be continued for 2 to 3 hours at the boil.

'Straw' is more difficult to dye than 'chip,' on account of the highly silicious character of the surface. The straw should be steeped for several hours in warm water before dyeing. Blacks are usually obtained with logwood and iron, but for colours the *direct cotton* and the *basic dyes* are chiefly used.

MATERIALS USED IN DYEING OPERATIONS.

A great variety of chemical substances are used in dyeing processes—acids, alkalis, oxidising and reducing agents, metallic salts, and a wide range of organic bodies. Two groups only need be here considered, viz.: (*a*) *mordants*, and (*b*) *colouring matters*.

Mordants. The function of a mordant is to chemically combine with the dyestuff employed, and fix the latter upon the fibre. It has already been mentioned that many colouring matters do not require the aid of mordants, but dye direct from their solutions. This applies to the *acid*, *direct*, *basic*, and *vat* dyes when used for wool and silk, and the *direct* and *vat* dyes when used for cotton. On the other hand, the *mordant* and *acid-mordant* dyes (as their name implies) demand the use of mordants on wool, as do the *mordant* and the *basic dyes* on cotton.

It is evident that the chemical properties of the dyestuff will govern the character of the mordant required for its fixation, and two types of mordants may thus be distinguished: (1) the *metallic* or *basic mordants*, used for the *mordant dyes*; and (2) the *acid mordants*, required in applying the *basic dyes* to cotton or other vegetable fibre.

Basic mordants are employed for fixing on animal and vegetable fibres those colouring matters which are of an acid character, *i.e.* either true acids or bodies containing hydroxyl-groups, of which the hydrogen is replaceable by metals. They are metallic salts, of which the most important are certain compounds of chromium, aluminium, iron, and tin.

Wool is mordanted by boiling it with dilute solutions of these metallic salts, usually with the addition of certain acids or acid salts, *e.g.* cream of tartar, sulphuric acid, formic acid, oxalic acid, &c. During this operation, the wool assists in the dissociation of the metallic salt, an insoluble basic salt being fixed within and upon the fibre, while a more acid salt remains in solution. The acids or acid salts, which are added along with the metallic salt, possibly assist the dissociation of the latter by forming more sensitive salts (tartrates, oxalates, &c.), and may be conveniently termed *assistants*.

As a rule, the mordanting operation precedes that of dyeing; not infrequently, however, the two operations take place simultaneously, and the dyeing is thus effected by the so-called 'single-bath' or 'one-dip' method, as, for example, in producing cochineal scarlet on wool. In such cases, the wool is boiled in a solution containing colouring matter, metallic salt, and assistant, in certain accurately determined relative proportions. Combination takes place between the colouring matter and the mordant, but the pigment which would otherwise be precipitated, is retained in solution by the liberated acid of the mordant or the assistant present, and is only gradually withdrawn from solution by the fibre, which thus becomes dyed.

In the case of the 'acid-mordant' dyestuffs, the application of the mordant follows that of the colouring matter.

Silk is mordanted in the same manner as wool, by boiling with metallic salt solutions; or, more usually, it is steeped for about 12 hours in cold solutions of the mordants previously rendered more or less basic and sensitive. By subsequently washing with (calcareous) water, the metallic salt absorbed by the silk is dissociated, and an insoluble basic salt is precipitated within the fibre.

Cotton is mordanted with metallic salts by processes very different from those adopted for wool and silk, since it has not the property of causing the dissociation of the metallic salts when boiled in their solutions. The methods adopted also vary according to the form of the material, *i.e.* whether it be cotton wool, yarn, or cloth.

With calico, it is usual to impregnate the fabric with solutions of metallic *acetates*, then to dry it, and expose for several hours to a moist warm atmosphere. During this so-called 'ageing' process, dissociation of the salt takes place, acetic acid escapes, and a more or less basic salt remains fixed upon the fibre.

Sometimes the 'ageing' is replaced by a 'steaming process,' in which the fabric is exposed from ½ to 1 hour to the action of high or low pressure steam in a closed chamber. This method is adopted by the printer of textile fabrics in the so-called 'steam style,' in which a mixture of colouring matter and metallic salt (usually acetate) is printed upon the fabric, which is then dried and steamed. The metallic salt is decomposed, a basic salt is precipitated upon the fibre, at the same time combining with the colouring matter and producing the coloured pigment. This method is analogous to the single-bath process of the woollen dyer.

Cotton may also be mordanted by impregnating it with a metallic salt solution, drying, and then passing through a solution of an alkaline substance to neutralise the acid and precipitate upon the fibre a basic salt or metallic oxide, *e.g.* ammonia, chalk, sodium carbonate, &c. Solutions of an alkali salt, the acid of which forms an insoluble compound with the base of the mordant, *e.g.* sodium phosphate, silicate, arsenate, &c., are also employed. All substances used in this manner for fixing the mordant upon the fibre are termed *fixing agents*.

In some cases of mordanting, the cotton is impregnated with the fixing agent first (*e.g.* tannic acid, sulphated oil, &c.), then dried and passed through the mordant solution afterwards, as for example, in Turkey-red dyeing.

Special methods of mordanting cotton are occasionally adopted, in accordance with the properties of the metallic salt employed. Stannic oxide, for example, may be fixed on cotton by passing the fabric through a solution of sodium stannate, and then through dilute sulphuric acid, and finally washing. Alumina is precipitated on the fibre by the mere exposure to air of cotton impregnated with sodium aluminate, in which case atmospheric carbonic acid is the active fixing agent.

The *chromium mordants* are of the first importance, since, with different colouring matters, they yield a considerable range of colours which are remarkable for their permanence. The most important chromium mordants are potassium and sodium dichromates, and they are more largely used as mordants in wool dyeing than any other metallic salts. In cotton dyeing they are not used as mordants, but are frequently employed as oxidising agents, *e.g.* to develop the colour in dyeing

catechu brown or aniline black, and are also used in producing chromate of lead yellow and orange. Chromium fluoride ($CrF_3,4H_2O$) is also used to a limited extent as a mordant for wool. Other chromium salts employed as mordants, chiefly for cotton, are chrome alum and chromium acetate. Chrome alum is obtained in large quantities as a by-product during the manufacture of alizarin; chromium acetate is prepared by mixing together solutions of chrome alum and lead acetate.

Wool is mordanted with chromium by boiling for 1–1½ hours with 3 p.c. potassium (or sodium) dichromate. In many cases it is beneficial to add 1 p.c. sulphuric acid (sp.gr. 1·84) or 1·5 p.c. hydrochloric acid (sp.gr. 1·16), or 6 p.c. tartaric acid, or 1 to 2 p.c. formic acid, whereby fuller or brighter colours are ultimately obtained. When potassium dichromate alone is employed, partial decomposition of the salt occurs, accompanied by some reduction, the wool absorbing some chromic acid and chromium chromate as well as potassium dichromate. When an addition of sulphuric acid is made, the wool absorbs only chromic acid. In both cases the mordanted wool has a yellow or buff colour, and only in the dye-bath does the reduction to the real mordanting body, chromic oxide, take place within the fibre through the interaction of the colouring matter. When formic or tartaric acid is the assistant employed, the mordanted wool has a green colour, reduction of the chromic acid taking place already in the mordanting bath, and chromic hydrate being deposited within the wool. If large amounts of potassium dichromate are employed in mordanting, especially if sulphuric acid is also added to the bath, bad results may be obtained through the colouring matter being oxidised and destroyed by the excess of chromic acid present in the wool. This defect is known as 'over-chroming.' In certain cases, potassium dichromate may be usefully applied in the same bath with the colouring matter (*e.g.* with alizarin), or by an after process (*e.g.* in the case of camwood).

Silk is not usually mordanted with chromium. It becomes mordanted, however, if boiled with a solution of potassium dichromate and tartaric acid after the manner of wool, but not if potassium dichromate alone, or with the addition of sulphuric acid, is employed.

Cotton may be mordanted with chromium by impregnating it with a more or less concentrated solution of chrome alum, drying, and passing through a boiling solution of sodium carbonate (100 grams per litre) or caustic soda. Better results are obtained by the use of 'chromium mordant G. A. I.' or 'G. A. II.' (M. L. & B.), which are chromium chromates. Other satisfactory mordants for cotton are chromium bisulphite (Knecht) and sodium chromite (Koechlin). A method in vogue with the printer is to impregnate (pad) or print the cotton with a mixture of colouring matter and chromium acetate, dry and steam ('steam colours').

The chief *aluminium mordants* employed for *wool* are aluminium sulphate and alum. The best results are usually obtained by merely boiling the wool for 1–1½ hours with a solution of 8–10 p.c. of the aluminium salt, with the addition of cream of tartar, in the proportion of 3 mols. to 1 mol. aluminium sulphate. Aluminium tartrate also gives excellent results, but it is cheaper to allow this salt to be formed in the mordanting bath itself in the manner described. With some colouring matters, oxalic acid or potassium binoxalate are to be preferred as assistants to cream of tartar.

Silk is mordanted by boiling with dilute aluminium sulphate solution, or by steeping 24 hours in a concentrated solution, and then washing in water, preferably calcareous.

The methods of mordanting *cotton* with aluminium are various. It may be impregnated with a more or less concentrated solution of alum or aluminium sulphate, dried, and then passed for a few minutes into a hot solution of sodium phosphate, arsenate, or silicate or ammonium carbonate. Or the cotton may be impregnated with a cold solution of neutralised sulphated oil, or of tannic acid, then dried, and steeped in a solution of aluminium acetate or basic aluminium sulphate. Another method consists in impregnating the cotton with a solution of sodium aluminate, drying and exposing to the air, or passing through a solution of ammonium chloride. Normal and basic aluminium acetates are also employed, the cotton being impregnated with their solutions, then dried, and exposed to a moist warm atmosphere ('ageing'), and finally passed through a hot solution of, *e.g.*, sodium arsenate. The aluminium acetates employed are prepared by dissolving alumina hydrate in acetic acid, or by decomposing a solution of aluminium sulphate with calcium or lead acetate ('red liquor'). As a general rule, the more basic the aluminium salts are, the more readily do their solutions precipitate by heating or on dilution with water, and the larger is the quantity of alumina they yield to the fibre when used as mordants.

The chief *iron mordants* employed are ferrous sulphate and acetate, and ferric sulphate, acetate, and nitrate.

The ferrous acetate employed is made by dissolving scrap iron in pyroligneous acid. The 'pyrolignite of iron' or 'black iron liquor' thus obtained is preferable to that made by the mutual decomposition of ferrous sulphate and lead acetate solutions; it is less liable to oxidise because of the presence of tarry matter and reducing agents, *e.g.* pyrocatechol, &c. Ferric sulphate is prepared by heating a mixture of definite proportions of ferrous sulphate, sulphuric acid, and nitric acid. Although the last-mentioned substance is only used as an oxidising agent, the final preparation is generally termed by dyers 'nitrate of iron.' The so-called 'pure nitrate of iron' (ferric nitrate) is prepared by dissolving scrap iron in nitric acid.

Wool may be mordanted by boiling in a solution of 7 p.c. ferric sulphate [$Fe_2(SO_4)_3$] and 4 p.c. potassium binoxalate, but iron is now very little used as a mordant for wool.

Silk may be mordanted by steeping for about 12 hours in a cold solution of pyrolignite of iron (sp.gr. 1·025), and afterwards washing well. The most usual mordant, employed largely in black-silk dyeing, is the basic ferric sulphate $Fe_4(SO_4)_5(OH)_2$. The silk is steeped in a somewhat concentrated solution of this salt (sp.gr.

1·25) for about 1 hour, then squeezed and well washed. The operations are repeated seven or eight times, after which the silk is boiled in an old soap-bath and finally washed. In this process, the very sensitive basic ferric sulphate absorbed by the fibre is decomposed during the several washings, a still more basic and insoluble salt being precipitated within the fibre.

Cotton is usually mordanted with iron by first impregnating it with a cold solution of tannin matter (*e.g.* myrobolans), and then, with or without drying, passing into a dilute solution of ferrous acetate, ferric sulphate, or nitrate (sp.gr. 1·01–1·02). The cotton may alternatively be impregnated with ferrous or ferric acetate, dried, and exposed to a moist warm atmosphere ('ageing'), and finally fixed by passing through a hot solution of, *e.g.*, sodium phosphate.

Tin mordants are now rarely used, but if required the stannous salts are employed for *wool* and the stannic salts for *cotton*. The chief stannous mordant is stannous chloride or 'tin crystals.' It is frequently sold as a somewhat acid solution under the names of 'single muriate of tin' (sp.gr. 1·3), or 'double muriate of tin' (sp.gr. 1·6). The general name 'tin spirits' is given to a variety of solutions of tin in mixtures of hydrochloric, sulphuric and nitric acids.

Wool is mordanted by boiling in a solution containing 6 p.c. of the weight of wool of stannous chloride, and 6–10 p.c. cream of tartar. Large proportions of stannous chloride should be strictly avoided, otherwise the dyed wool feels harsh and its general properties are impaired.

Silk may be mordanted in the same manner as wool, or steeped several hours in a more or less concentrated solution of stannic chloride, and then well washed.

Cotton is mordanted with stannic oxide by impregnating the cotton with cold tannin solution (*e.g.* sumach) for 3 hours, then squeezing, and, with or usually without drying, steeping 1 hour in a dilute solution of stannic chloride (sp.gr. 1·02), and washing. Cotton thus mordanted was much used formerly for fixing mordant dyes—peachwood, logwood, &c., in which case the stannic oxide constituted the mordant, the tannic acid acting as fixing agent. Now that the basic coal-tar dyes are so much employed in dyeing cotton, although the same method of mordanting is employed, the *rôles* of the tin salt and tannic acid are reversed, for it is really the tannic acid which is the essential mordant, while the stannic chloride serves only as the fixing agent.

Acid mordants are employed for fixing basic colouring matters on cotton. They are not used for this purpose in wool and silk dyeing, since these fibres themselves act as acid mordants, and are dyed directly without the aid of any external mordant.

Tannic acid is the mordant *par excellence* for fixing the basic coal-tar colours on cotton. This fibre absorbs tannic acid from its cold solution, and if, when thus prepared, it is immersed in a solution of a basic colouring matter, the tannic acid combines with the colour base, a coloured lake is formed within the substance of the fibre, and the cotton becomes dyed. During the dyeing process, the acid originally in combination with the colour base is displaced, and since in the free state it interferes with the complete formation of the colour lake, it is found beneficial to add a small proportion of sodium carbonate or acetate to the dye-bath. Since the tannates of colour bases are somewhat soluble, in excess of tannic acid or in alkaline solutions, it is necessary in practice to fix the tannic acid on the fibre, previous to dyeing, in the form of an insoluble metallic tannate. This is done by passing the tannic acid prepared cotton through a hot or cold solution of tartar emetic or stannic chloride; tannate of antimony or tin is thus fixed on the fibre, and these salts have as great an attraction for the colour base as free tannic acid has. Cotton thus mordanted and dyed is probably permeated with a very insoluble double tannate of antimony or tin and colour base, a triple compound which is insoluble in alkaline solutions, and therefore fast to washing with soap, &c.

The tannin mordants, chiefly used by the dyer, are gall nuts and sumach, for light colours; and myrobolans, divi-divi, quebracho, and chestnut extract, for dark colours.

As already pointed out, tannic acid is sometimes used as a *fixing agent* for tin, iron, or aluminium mordants, and since its iron compound is of a bluish-black colour, it sometimes serves as a useful *colouring matter*.

Tannic acid is not used as a mordant for wool, but for *silk* it is largely employed, partly for adding weight to the silk, and partly for the purpose of dyeing it black in conjunction with iron mordants. Its utility as a weighting agent is owing to the fact that under suitable conditions silk absorbs as much as 25 p.c. of its own weight of tannic acid from a hot solution, whereby the fibre gains not only in weight, but also in volume.

Fatty acids are used as mordants very much in the same way as tannic acid for fixing the basic coal-tar colours on cotton. They are, however, not attracted by cotton from their solutions, but they form insoluble lakes with the colour bases. The method of procedure is to impregnate the cotton with a more or less concentrated solution of their alkali salts, *e.g.* soap; after drying, the fabric is passed through, or preferably steeped in, a cold solution of aluminium sulphate, and washed. Although the fatty acid is thus fixed on the fibre as an insoluble aluminium soap, it is still capable of combining with the colour base when the cotton is passed into a solution of a basic colouring matter. Colours dyed by this method are brighter than, but not so fast to washing as those fixed by means of tannic acid.

Instead of ordinary soap, a more convenient fatty-acid mordant to employ is the so-called 'sulphated oil.' This is prepared, by mixing two parts by weight of castor oil with about one part of sulphuric acid (sp.gr. 1·84), and allowing the mixture to stand for 24 hours. It is then washed with a strong solution of common salt to free it from excess of acid, and is finally neutralised with ammonia or caustic soda. The product of the action of the acid upon the oil is somewhat complex, but its practical utility depends upon the fact that it behaves like a fatty acid and gives an extremely soluble soap with alkalis. Ordinary castor-oil soap produced by boiling the oil with caustic soda is also very soluble, and may be used as a mordant.

Sulphated oil is frequently called 'Turkey-red oil,' 'alizarin oil,' and 'soluble oil,' since it is largely used in the modern short process of Turkey-red dyeing as the fixing agent for the necessary aluminium mordant, and it gives the characteristic brilliancy of colour obtained by the use of the oil preparations formerly employed. Monopole oil is a similar product.

Phenolic colouring principles, *e.g.* alizarin, and certain acid colouring matters derived from benzidine, stilbene, fluorene, &c. (the direct cotton dyes) can also be fixed on cotton, and serve as mordants for basic colouring matters, but they are only occasionally used for this purpose for the production of compound shades.

Colouring Matters.

(For Classification, see p. 282.)

General Methods of Application.

Class I.—Mordant dyes. This group of dyestuffs includes the majority of the *natural dyes*, also the numerous class of *alizarin dyes*, a number of derivatives of *pyrogallol* and other *phenols*, and certain *quinone-oximes* or *nitroso- dyes*. The following are the chief members of the group: *mordant dyes of natural origin*—logwood; madder; cochineal; limawood and other 'soluble redwoods'; camwood and other 'insoluble redwoods'; fustic; weld; quercitron bark and flavin.

Synthetic mordant dyes.—Alizarin; anthrapurpurin, flavopurpurin, and purpurin; nitroalizarin (alizarin orange); alizarin maroon (aminoalizarin); alizarin bordeaux; anthracene brown; alizarin blues; alizarin cyanins; anthracene blues; alizarin greens; cœrulein; anthracene yellow; mordant yellow, galloflavin, &c.; alizarin black; gallein; gallocyanin; cælestine blue; naphthol green, dark green, gambine, &c.

The mordant dyes are largely used in the dyeing of wool and in the dyeing and printing of cotton and silk. Generally speaking, they yield colours which are of great fastness to light, soaping, acids, alkalis, bleaching agents, &c. As regards cotton dyeing, they are now being replaced by the very fast vat dyes introduced within the past few years.

When a fabric, previously mordanted with a metallic salt, is dyed with a mordant dye, a chemical reaction takes place, resulting in the formation of a new compound which is the actual colouring substance; this compound being, at the same time, fixed upon the fibre, which thus becomes dyed. These *colour lakes* or *pigments* may, for the most part, be equally well produced by bringing together the mordant and the dyestuff under suitable conditions in the absence of the fibre. Many colour lakes of this class are indeed manufactured in bulk for use as painters' pigments, &c.

There are three methods by which mordant dyes may be applied: (1) the mordant may be first applied to the fibre, and afterwards the dyestuff in a separate operation ('mordanting and dyeing method'); (2) the order of application of mordant and dye may be reversed ('dyeing and saddening method'); or (3) the mordant and dyestuff may be applied simultaneously ('single-bath method'). All these methods are in use. If equally good results can be obtained, the 'single-bath' process is to be preferred, but usually the 'mordanting and dyeing' process gives the maximum fastness.

The dyeing of wool with mordant dyes.—When potassium dichromate is employed as mordant, the '*mordanting and dyeing*' process is usually preferable, because, in the 'single-bath' process, the acid necessarily added to dissolve the colour lake formed in the dye-bath, converts the mordant into such a powerful oxidising agent by liberating chromic acid, that most dyestuffs are injuriously affected. In the two-bath process, the wool should be thoroughly washed after mordanting. If this operation is omitted, a portion of the mordant passes from the wool into the dye-bath, and, combining with an equivalent amount of colouring matter, forms a precipitate which floats about in an insoluble condition. This not only leads to loss of dyestuff, but also tends, by superficial absorption, to cause the dye to 'rub off.' The dyeing process consists in boiling the wool for from 1 to 2 hours with the colouring matter in aqueous solution. The final washing, after dyeing, has for its object the removal of any colouring matter which is imperfectly fixed; but, however thorough the washing may be, there is usually a small amount of colouring matter present on the dyed wool, which has merely been absorbed without combining with the mordant. This free colouring matter will dissolve out or 'bleed,' during milling or scouring, because most mordant dyes are readily soluble in alkaline solutions. A slight supplementary mordanting ('afterchroming') is frequently given to fix this small amount of free dyestuff.

The '*dyeing and saddening*' method is not much used with the true mordant dyestuffs, but is the chief process used in applying the *acid mordant dyes*. Since the ultimate intensity of colour depends chiefly upon the amount of dyestuff which is fixed in the first bath, whilst the colour is only developed by the mordant in the second bath, it is obviously more difficult to exactly match a pattern when this process is used than when the mordant is applied first.

In the '*single-bath*' method of dyeing, the bath is prepared with the necessary amount of mordant and dyestuff with an addition of sufficient acid (usually oxalic or acetic acid) to dissolve the colour lake formed. This process is therefore only suitable when the colour lake is soluble in dilute acid, and this is particularly characteristic of the tin and aluminium colour lakes; although the single-bath process is also frequently applicable in the case of ferrous sulphate or chromium fluoride mordants.

The dyeing of silk with mordant dyes.—The mordant dyes are not very largely used on silk, chiefly because they detract somewhat from the lustre of the fibre. The degree of fastness of the acid dyes, if suitably selected, is, moreover, usually sufficient for the requirements of the silk dyer. The methods of mordanting have already been dealt with. Dyeing must take place at the boil for about an hour, and the silk is subsequently brightened by working in a warm dilute solution of acetic or tartaric acid, and dried without washing.

Dyeing of cotton with mordant dyes.—The 'mordanting and dyeing' method is generally used in cotton dyeing. Aluminium is the chief mordant employed, and, in conjunction with

alizarin, it yields the important Turkey-red dye. This is a complex compound containing an alizarin-aluminium-calcium lake in combination with oxidised fat acids. In the production of this colour, the cotton is first prepared with sulphated oil, then dried, mordanted with alum, and subsequently dyed with alizarin. The complete process involves a large number of operations, for the details of which manuals of dyeing must be consulted. The dyeing of Turkey red is a very ancient process, having been carried out centuries ago in India by the aid of milk (as fatty matter) and munjeet, the Indian madder plant. No alum was employed, but the plant with its earthy incrustations contained sufficient alumina to form the alumina lake. The art spread from the East through Persia to Turkey, and was first introduced into this country (Glasgow) in 1790. Madder has now been entirely replaced by synthetic alizarin in Turkey-red dyeing, and the substitution of sulphated oil for olive oil or soap has also greatly simplified the process.

Another important mordant dye on cotton is logwood black, which is obtained by dyeing with logwood on tannin-iron mordant. It is largely used in hank and warp dyeing. Catechu brown is produced by the 'dyeing and saddening' method, the cotton being first steeped in a strong solution of catechu, and subsequently treated with potassium dichromate. The latter acts essentially as an oxidising agent, producing the so-called *japonic acid* on the fibre.

A great variety of permanent and bright colours may be obtained with mordant dyes on cotton mordanted with chromium or aluminium, but they are not very largely used, fast colours being chiefly produced by means of the *sulphide, vat,* and *ingrain* dyes (Classes VI., VII., VIII.).

Class II.—**Acid-mordant dyes.** These dyes are suitable only for wool and silk, and are largely used on wool. They are now very numerous, and are chiefly azo- compounds containing salicylic acid or orthoaminophenol components. Some, however, are anthracene or pyrogallol derivatives. Unlike the mordant dyes, they usually contain sulphonic acid groups.

Many of the acid-mordant dyes may be employed as ordinary acid dyes, since a mordant is not essential to the development of their colour. Usually, however, such dyestuffs produce faster colours when applied in conjunction with a mordant.

An exhaustive list of acid-mordant dyestuffs cannot be given, but the following will serve as examples. They include dyes giving a complete range of colours. *Reds*: acid alizarin, anthracene, chrome, cloth and milling reds. *Oranges and yellows*: cloth oranges and yellows, alizarin yellows (certain marks are mordant dyes), chrome yellows, milling orange and yellow, diamond and mordant yellow. *Greens*: acid alizarin, chrome, diamond and milling greens. *Blues*: acid alizarin, brilliant alizarin and chrome blues; alizarin sapphirole; cyananthrol; chromotropes (chromotropes dye red as acid dyes). *Violets*: alizarin heliotropes; anthraquinone and chrome violets; fast violet. *Blacks and greys*: acid alizarin, acid chrome, anthracene acid, anthracene chrome, chrome, chromotrope and diamond blacks. *Browns*: acid alizarin, acid anthracene, chrome, cloth, diamond, and palatine browns; chromogen.

Dyeing of wool with acid-mordant dyestuffs.—The usual method of application of this class of dyestuffs is to prepare a bath containing the necessary amount of dyestuff along with 1 to 3 p.c. sulphuric or 3 to 5 p.c. acetic acid, and 5 to 10 p.c. sodium sulphate (Glauber's salt). After the solution has been brought gradually to the boiling-point, the boiling is continued until the colouring matter is entirely fixed, an additional amount of acid being added if necessary. Excess of acid, however, frequently retains the dyestuff in solution. The wool is then removed from the bath, the metallic salt is added, and the wool is again boiled in the bath for half an hour. In most cases, potassium dichromate, to the extent of one-half the weight of the dyestuff, is the mordant employed.

A modification of this process is used with the *metachrome* series of dyestuffs. The *metachrome mordant* is a mixture of yellow potassium chromate and ammonium sulphate. The bath is prepared with 3 to 5 p.c. of this mordant together with the dyestuff. A prolonged boiling is necessary, during which the ammonium salt is decomposed, ammonia being evolved and the liberated sulphuric acid gradually converts the chromate into dichromate and assists in the fixation of the dye and the formation of the colour lake.

The *anthracene chromate dyes* are applied in a bath containing colouring matter, dichromate, and sodium sulphate; this being another modification of the usual process.

The mercerol and autochrome dyes are also applied by special processes.

The acid-mordant dyes are of increasing importance in wool dyeing, but are little used on silk, and not at all on cotton.

Class III.—**Acid dyestuffs.** The acid dyes constitute by far the most numerous class of synthetic colouring matters. The chief chemical groups of acid dyes are *azo-dyes, nitro-compounds, sulphonated basic dyes,* and *phthaleins*; the greatest number being azo- dyes. The azo- dyes contain few greens, blues, and violets; but the reds, oranges, yellows, browns, and blacks are very numerous. The nitro- compounds are few in number and are all yellows, the chief being picric acid and naphthol yellow. The greater number of the sulphonated basic dyes, on the other hand, are greens, blues, and violets, but acid magenta belongs to this group. The resorcin or phthalein dyes are chiefly brilliant pinks or reds, the eosins being the most important group.

So extremely numerous are the acid dyes, and their names are so varied, that no useful purpose would be served by further enumeration of a small number of the products.

The dyeing of wool with acid dyes.—The commercial acid dyes are, in most cases, the sodium salts of sulphonic acids. The nitro-compounds, however, owe their acid character to the presence of nitro- groups in the molecule.

The simplest and most usual method of dyeing acid colours on wool is to prepare a bath containing the requisite amount of dyestuff with 1 to 4 p.c. of sulphuric acid and 10 to 20 p.c. of sodium sulphate (Glauber's salt). The wool is dyed in this solution for about an hour.

boiling for the greater part of the time. Some dyes require smaller, and some larger percentages of acid. The sodium sulphate exerts a levelling influence on the fixation of the dyestuff, probably by reason of the solvent action which it exerts, since acid dyes are readily removed ('stripped') from wool by boiling in a solution of sodium sulphate. Another reason is to be found in the retarding action which it exerts in the liberation of the free colour acid by the sulphuric acid. The equation, which may be expressed as:

Colour salt + $H_2SO_4 \rightleftarrows$ colour acid + Na_2SO_4,

is reversible.

Sodium bisulphate may be used in place of the sulphuric acid and sodium sulphate, or the sulphuric acid may be entirely replaced by acetic or formic acid.

In the case of dyestuffs which do not readily produce level colours on the fabric, the acid may be added to the bath, gradually in small portions at a time, or may be substituted by an ammonium salt, *e.g.* ammonium sulphate or acetate. The acid is then liberated very gradually as the ammonium salt is decomposed in the boiling bath, and the colouring matter is therefore converted very slowly from the condition of the soluble sodium salt to that of the more or less insoluble free sulphonic acid.

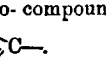
The dyeing of silk with acid dyes.—Acid dyes are very largely used in silk dyeing. They are applied in a bath containing a large quantity (up to 25 p.c. in volume) of 'boiled-off' liquor, the soapy solution of the silk gum obtained in the 'ungumming' of raw silk. The bath is rendered slightly acid by means of sulphuric, acetic, or formic acid. Dyeing usually takes place at 80°–90°, at which temperature silk has more affinity for acid dyes than in a boiling bath.

After dyeing, the silk is washed and is then 'brightened' by working in a dilute (sulphuric, acetic, or tartaric) acid solution and dried without washing.

The dyeing of cotton with acid dyes.—There is no satisfactory method of fixing the acid dyes upon vegetable fibres.

Class IV.—**The direct dyes.** The direct dyes have the special property of dyeing cotton without the aid of a mordant. Like the acid dyes, they are for the most part azo- compounds, but contain the chromophor —N=N— twice in the molecule, and thus constitute the tetrazo-group of azo- dyes. They further resemble the acid dyes in that they are alkali salts of sulphonic acids, but as regards dyeing properties, they differ greatly from the simpler azo-acid dyes. Since the introduction, in 1884, of the first of the direct dyes, a very large number have been placed on the market, and the group contains dyes of all colours—reds, oranges, yellows, greens, blues, violets, browns, and blacks. As examples of these dyes may be mentioned the congo, benzo, diamine, mikado, titan, and hessian dyes.

Primuline is an example of a direct dye which is not an azo- compound. It contains the



chromogen.

Turmeric is the only important natural direct dye for cotton.

The direct dyes are applicable to all fibres, but are rarely used on silk. No satisfactory explanation has been given of the fact that they readily dye cotton, whereas the acid dyes are entirely devoid of this property. The further fact that the direct dyes dye wool in a neutral, or even slightly alkaline bath, whereas the acid dyes require the addition of acid, also demands explanation.

The dyeing of wool with direct dyes.—These colouring matters are applied to wool in a neutral or feebly acid bath with or without the addition of sodium sulphate (Glauber's salt). In some cases, an after-treatment with a metallic salt gives improved fastness, the dyes then practically falling into the class of acid-mordant dyes.

As a class, the direct dyes on wool are much faster to milling than the ordinary acid dyes. When fixed on wool, they are also faster to acids, washing, and light than when dyed on cotton. In some cases, the colour produced by a direct dye on wool and cotton is identical, in other cases it differs considerably.

The dyeing of silk with direct dyes.—These dyes are not largely used on silk. They are applied in a similar manner to the acid dyes, but smaller amounts of 'boiled-off liquor' and acid are required.

The dyeing of cotton with direct dyes.—The application of the direct dyes to cotton is very simple. They are dyed either from a cold, lukewarm, or boiling solution, to which is added a small amount (up to 2 p.c.) of sodium carbonate, and an amount of a neutral salt (up to 20 grams NaCl or Na_2SO_4 per litre), which is governed by the solubility of the dyestuff employed. At low temperatures more concentrated solutions of colouring matter are required. Brighter colours are obtained by passing the dyed material through a solution of Turkey-red oil before drying or by adding this substance to the dye-bath.

Mercerised cotton has a much greater affinity than ordinary cotton for the direct dyes, and in dyeing this fibre special precautions are necessary to produce level colours.

Many of the direct dyes produce on cotton colours of great brilliance and richness, but they bleed out into hot water, and are still more readily attacked by soap. Most of them are also comparatively fugitive to light.

There are two processes by means of which the fastness properties of certain of the direct dyes can be improved.

1. *The diazotising and developing process.*—This process is applicable only in the case of those dyestuffs in which amino- groups constitute the auxochrome. The cotton is first dyed by the general process above described, then washed, and afterwards worked for a few moments in a cold dilute solution of nitrous acid (2 p.c. $NaNO_2$ and 4 p.c. H_2SO_4 on the weight of the cotton). This treatment diazotises the amino- groups. The cotton is then well washed in cold water and entered immediately into the developing bath, which contains a solution of a phenolic or amino- compound; sufficient alkali or acid respectively being added to bring the 'developer' into solution. The chief developers used are phenol, resorcinol, α- or β-naphthol, aminonaphthol, aminodiphenylamine, *m*-tolylenediamine, and certain of the naphthol sulphonic acids.

Primuline is applied by the process just described.

A modification of this method is known as the '*coupling process.*' The cotton is first dyed with the direct dye, and, after rinsing, is worked in a diazotised solution of the 'coupler.' The chief body used as coupler is *p*-nitraniline. Ready prepared stable diazo- compounds of this base are sold under the names 'nitrazol,' 'azophor red,' and 'nitrosamine red.'

2. *After-treatment with metallic salts.*—In this process for improving the fastness of the direct dyes on cotton, the fibre is first dyed in the ordinary way, and then, after rinsing, is treated for half an hour in a warm acid solution of a suitable metallic salt. The salts chiefly employed are copper sulphate, potassium dichromate, and chromium fluoride; from 1 to 3 p.c. with addition of 2 to 4 p.c. of acetic acid being used. A mixture of the two first-mentioned salts is frequently used. This process is mainly employed in the case of blues, browns, and blacks. The chromium salts exert the chief influence in increasing the fastness to washing, and the copper salt the fastness to light.

This process is only applicable to the case of dyestuffs containing free OH or COOH groups.

Cotton dyed with direct dyes may be 'topped' with basic dyes, for which the direct dyes act as mordants.

CLASS V.—**The basic dyes.** This group of colouring matters is numerically smaller than the mordant, acid, or direct dyes. It includes, however, the most brilliant dyes known, rhodamine pink, auramine yellow, malachite green, methylene blue, and methyl violet being well-known examples.

The basic dyes are very diverse in their chemical constitution. Many are derivatives of di- or tri-phenylmethane (magenta, malachite green, methyl violet); others are azo- compounds (chrysoidine, Bismarck brown); some are azine-derivatives (safranine and induline); and others contain sulphur as an essential constituent (methylene blue).

The commercial basic dyes are usually hydrochlorides of the colour bases, but some are acetates, oxalates, sulphates, or zinc chloride double salts. They are characterised by great tinctorial power, 1 p.c. being usually sufficient to produce a full rich colour. As a class, they are not fast to light.

The dyeing of wool with basic dyes.—These dyes are little used on wool, the acid dyes being applied in an equally simple manner and producing faster colours. Wool has a strong affinity for basic dyes, and readily becomes dyed if immersed in their solutions. A small amount of sulphuric or acetic acid may usually be added with advantage. Certain of the basic dyes, *e.g.* Victoria blue, are very fast to milling when dyed on wool, and such are still employed.

The dyeing of silk with basic dyes.—Members of this group of colouring matters are largely used by the silk dyer when fastness to light is not important. The silk yarn is dyed at 60°–80° in the colour solution, to which may be added some 'boiled-off liquor' or neutral soap. After rinsing, the dyed silk is brightened in a dilute solution of acetic or tartaric acid.

The dyeing of cotton with basic dyes.—Cotton has little affinity for basic dyes, which, on this fibre, must therefore be applied in conjunction with a mordant, and since the dyestuffs of this class are basic in character, the mordant must be of an acid nature.

Three types of acid mordants are available, viz.: tannin matters, fat acids, and colour acids.

1. *Tannin mordants.*—As mentioned in dealing with the mordants, cotton has a natural affinity for tannic acid, which it withdraws from solution. Since tannic acid forms lakes with the basic colouring matters, cotton thus prepared may be dyed with basic dyes, but the colours produced in this manner are not fast against washing. As previously explained, however, if after mordanting with tannin the cotton is treated with a salt of antimony, tin, or iron, an insoluble metallic tannate is formed on the fibre, which compound has the same affinity for basic dyes as tannic acid has. The fastness properties of the double tannate of colour base and metal are much superior to those of the simpler tannates of the colour bases.

For the production of pale or bright colours, commercial tannic acid, gall nuts, or sumac are the tannins employed. The cotton is saturated ('padded') with a solution of 2° to 3°Tw. strength, or steeped for 2 to 3 hours in a solution containing 2 to 5 p.c. tannic acid or 10 to 30 p.c. ground gall nuts or sumac; the amount being calculated on the weight of cotton. The yarn or fabric after squeezing is then at once passed into a 'fixing bath' containing 0·5 to 3 p.c. of tartar emetic or an equivalent amount of antimony oxalate or fluoride. After well washing, the cotton is dyed with 0·1 to 1 p.c. of basic dye.

Additions of acetic acid to the tannin bath, ammonium chloride and chalk to the fixing bath, and dilute acid to the dye-bath, are frequently made. The mordanting and fixing baths may be used for several successive lots of material.

If the brightest possible shades are not required, some cheaper tannin matter (myrobalans or quebracho) may be employed, and stannic chloride may replace tartar emetic as fixing agent. For dark shades, ferrous acetate ('black iron liquor') is used as fixing agent, the blue-black tannate of iron producing a composite colour with the basic dyestuff.

2. *Fatty mordants.*—If Turkey-red oil or soap is used as mordant, the colour produced with a given basic colour is brighter, but less fast than when tannin mordant is used.

The fat acids are fixed on the cotton as metallic salts, usually aluminium salts; the fibre being first saturated with a solution containing 1 lb. of sulphated oil or soap per litre, then dried and passed into a solution of aluminium acetate ('red liquor') at about 8°Tw.

3. *Colour acids as mordants.*—Mention has already been made of the fact that the direct dyes act as mordants towards the basic dyes, compound shades being thus obtained. Mordant, sulphide, and acid dyes also possess the property of attracting basic dyes, but these combinations are not much employed.

The dyeing of jute with basic dyes.—Although jute is a vegetable fibre, it does not consist of free cellulose, but of a bastose-cellulose compound, *corchorobastose* (Cross and Bevan). The dyeing properties of this substance differ materially from those of cellulose, jute, in fact, behaving in a very similar manner to tannin-mordanted cotton, and dyeing direct with basic dyes.

CLASS VI.—**The sulphide dyes.** The number

and importance of this group of dyes has extended greatly during the past few years. They are chiefly employed for the production of fast blacks on cotton and other vegetable fibres, but fast blues, greens, browns, and yellows may also be obtained. They come into the market in the form of powders, which are usually insoluble in water, but soluble in solutions of sodium sulphide. They are also rendered soluble by other reducing agents, *e.g.* sodium hydrosulphite or glucose in alkaline solution.

The sulphide dyes are commercially known under the following names: sulphur, sulphurol thiogene, thionol, thional, thioxine, cross-dye immedial, katigen, kryogen, pyrogen, pyrol rexoll, eclipse, vidal, or auronal dyes. They are produced by melting together under suitable conditions aromatic nitro-, amino-, or imino-compounds with sulphur and sodium sulphide. The constitution of the sulphide dyes is not known, but the commercial products are probably mixtures of polymers or homologues and not homogeneous bodies. They contain free sulphur in amount varying from 1 to as much as 12 p.c. (Gardner and Hodgson, J. Soc. Chem. Ind. 1910, 672), and also contain very variable amounts of sodium sulphide and polysulphides.

The dyeing of wool with sulphide dyes.—Wool is rarely dyed with sulphide dyes, on account of the injurious action of sodium sulphide on the fibre. The wool may be protected to some extent against this action by the addition to the dye-bath of glucose, tannic acid, or ammonium salts. A previous treatment of the fibre with formaldehyde has also been recommended (R. Kann, Eng. Pat. 3492, 1903), but this reduces the affinity of the wool for these dyestuffs.

The dyeing of silk with sulphide dyes.—Fast blacks, blues, and browns may be obtained on silk by the following process: The sulphide dyestuff, together with the necessary amount of sodium sulphide, and twice as much glucose as sulphide, is boiled in water until the dyestuff is dissolved. This solution is added to the boiling dye-bath already containing 1 gram soda ash, 3 c.c. Turkey-red oil, and 5 to 10 grams sodium sulphate per litre. The silk is dyed below the surface of the liquor for an hour, then rinsed, soaped, and brightened with acetic acid. Faster shades are obtained if the dyed silk is subsequently treated in a boiling solution containing 2 to 4 p.c. potassium dichromate and 3 to 6 p.c. acetic acid.

The dyeing of cotton with sulphide dyes.—This group of dyestuffs is now of the greatest importance in cotton dyeing for the production of fast blacks, and to a less extent, fast blues, greens, browns, &c. The necessary ingredients in the dye-bath, in addition to the dyestuff, are sodium sulphide, sodium sulphate, or other neutral salt, and an alkali, usually sodium carbonate. The actual and relative amounts of these substances vary considerably with different dyestuffs, depending upon the ease with which the colouring matter employed undergoes reduction and the solubility of the reduced product. An addition of Turkey-red oil, monopol oil, or glue, tends to produce more level and brighter shades; glucose aids the reduction. Dyeing takes place just below the boil, and it is usually desirable to keep the cotton completely immersed during the operation, in order to prevent irregular oxidation. The baths are used in a very concentrated condition, with the result that such a small proportion of the dyestuff is withdrawn, that for reasons of economy 'standing baths' are employed, that is, the baths are used continuously and replenished with dyestuff, &c., as required. The dyeing takes place in iron vessels, copper being rigidly excluded, on account of the ease with which it is attacked by sodium sulphide.

Some of the sulphide dyes do not require any treatment subsequent to dyeing other than exposure to air, but with many dyes of the group an after-treatment greatly improves their fastness to light and other influences. The chief object of the after-treatment is to ensure the complete oxidation of the colouring matter; and, as oxidising agents, chromium salts, or hydrogen peroxide are used. Steaming the material in presence of air is employed in the case of immedial blue.

After-treatment with potassium dichromate and acetic acid is now usually practised, since the use of copper salts has proved to be dangerous in regard to the subsequent tendering of the fibre on account of their catalytic action in inducing acid formation (Gardner and Hodgson, J. Soc. Chem. Ind. 1910, 676).

The tendering of cotton dyed with sulphide blacks has greatly retarded the use of these dyestuffs. The defect does not usually develop for some weeks or months after the material has been dyed, and it has been shown to be due to the slow formation of sulphuric acid on the fibre. The development of acid arises mainly from the oxidation of free sulphur present on the dyed fibre, but even in the absence of free sulphur, acid development may take place by decomposition and oxidation of the colour molecule.

The risk of tendering, during storage, of cotton dyed with sulphide blacks is entirely eliminated by a final treatment of the material, before drying, with sodium acetate; but, of course, the protective influence of this salt disappears if the material is washed.

CLASS VII.—**The vat dyes.** Until comparatively recently, indigo was the sole representative of this group of dyestuffs. The synthetic production of indigo was, however, followed by that of a number of derivatives of this body. Other series of vat dyes have also been introduced within the past few years, and by their use it is now possible to produce on cotton many bright colours of a degree of fastness hitherto unattainable.

The essential features of a vat dye are its easy reduction to a form soluble in dilute alkali, its attraction in this condition by the fibre, and its ready reoxidation on the fibre to the original insoluble condition. The reduced solution is termed the 'vat.'

The vat dyes include the following: indigo (indigotin); mono-, di-, tri-, and tetra-halogen derivatives of indigotin; methyl and tolyl indigotins; ciba dyes (brom indigotins); thioindigo red and scarlet; helindone dyes (sulphur derivatives); algole dyes; cibanone dyes, and the indanthrene dyes. The group includes dyes of all hues. The blues predominate in importance.

Indigo is the oldest and by far the most important of the vat dyes. It has been employed

in India for at least 3500 years, by methods not differing essentially from some of those which are still employed. It is used upon all fibres, but least commonly upon silk.

Various reducing agents are employed for the conversion of the insoluble indigo blue into indigo white, and they are always associated with an alkali to dissolve the latter substance. After saturating the fibre with the alkaline solution, the indigo white is reconverted into indigo blue upon the fibre by atmospheric oxidation.

The dyeing of wool with indigo vat blue.—The two chief indigo vats used for wool are the fermentation vat and the hydrosulphite vat, the former being chiefly used for dark shades on woollen cloth (Army and Navy cloth, &c.), and the latter for light colours on slubbing, yarn, &c. There are several forms of fermentation vat, of which the woad vat is the most important in this country. The precise composition and 'setting' of the vat is largely a matter of experience, the ingredients being somewhat as follows: finely ground indigo, 12 to 18 lbs.; woad, 300 lbs.; bran, 10 lbs.; madder, 12 to 18 lbs.; lime, 12 lbs.; water, 600 gallons. After warming the liquor, various fermentations set in, the essential bacterium being the *Desmobacterium hydrogeniferum*. The starchy matters present are first converted into glucose, which then splits up into lactic acid, the latter undergoing butyric fermentation with evolution of hydrogen.

Excessive fermentation is prevented by making suitable additions of lime, or it is accelerated, if necessary, by adding further quantities of bran.

In the so-called German or soda vat and the Indian or potash vat, the woad is replaced by bran with the addition of molasses, and the lime by sodium or potassium carbonate.

To avoid the derangements to which all fermentation vats are liable, Collin and Benoist (J. Soc. Chem. Ind. 1885, 493) proposed to employ a pure ferment and a completely fermentable food material; but this process has not come into practical use.

Natural indigo is still largely used in the fermentation vats, but in the hydrosulphite vat the synthetic product is generally employed. The hydrosulphite vat may be prepared as follows: synthetic indigo (20 p.c. paste), 10 lbs.; caustic soda solution 42°Tw., 3 pints; sodium hydrosulphite solution 20°Tw., 7½ gallons; water, 50 gallons. The liquid is heated to 50° until it becomes clear greenish-yellow. The solution of indigo white thus obtained is diluted to 250 gallons with water at 50°, to which a little hydrosulphite has been previously added.

The hydrosulphite solution may be replaced by 3 lbs. of solid sodium hydrosulphite, in which case the amount of caustic soda must be increased. 3½ lbs. of natural indigo (60 p.c. indigotin) are about equivalent to 10 lbs. of synthetic indigo (20 p.c. paste). After working in the vat, the goods are well squeezed, and then exposed to the atmosphere to oxidise the indigo white: they are then well washed.

Dark shades of indigo blue on wool are usually 'bottomed' with a red dye (diamine fast red or barwood) before vatting, and are frequently 'topped' after vatting with orchil or other dyestuff in order to add 'bloom' to the colour.

In most respects indigo vat blue is an extremely fast colour, but has the defect of being liable to 'rub off.'

The dyeing of silk with vat indigo.—This dye is not much employed on silk. If used, the most suitable vat to employ is the hydrosulphite vat set with synthetic indigo.

The dyeing of cotton with vat indigo.—The hydrosulphite vat is largely employed in cotton dyeing as well as in the dyeing of wool, but it is used cold in the case of cotton. Other cotton vats are the 'copperas vat' and the 'zinc-powder' vat.

A strong copperas vat contains, indigo (60 p.c.), 10 lbs.; ferrous sulphate, 30 lbs.; and quicklime 35 lbs., in about 200 gallons of water. The lime decomposes the ferrous sulphate, with the production of ferrous hydroxide, and this in the presence of lime and indigo decomposes the water, yielding ferric hydroxide and hydrogen; the latter at once combines with the indigotin and produces indigo white, which dissolves by reason of the excess of lime present. The normal colour of the vat liquor thus obtained is brownish-amber.

The zinc-powder vat is made up with water, indigo, zinc-powder, and lime. In the presence of the lime and indigo, the zinc decomposes the water even at the ordinary temperature, and the liberated hydrogen effects the reduction of the indigo.

Vat dyes other than indigo.—These may be roughly divided into two groups: (*a*) the *indigoids*, which may be considered as derivatives of indigotin; and (*b*) the *anthracene* derivatives. They all possess the common property of forming vats when treated with hydrosulphite of soda, but whereas the indigoids may be applied to the animal as well as to the vegetable fibres, the anthracene derivatives are only suitable for cotton on account of the large amount of caustic alkali required for their solution. The reduced anthracene vat dyes also do not appear to possess much affinity for wool.

(*a*) *Indigoids.*—The dyes of this series now on the market are: thioindigo red and scarlet; helindone red and scarlet; ciba red and scarlet; vat red; helindone orange and yellow; ciba green; brom indigos; ciba blues and greys; ciba violets and heliotropes; helindone brown. Some of the algole reds also probably belong to this group.

(*b*) *Anthracene vat dyes.*—Indanthrene red; algole reds; indanthrene yellows and oranges; algole yellows and oranges; cibanone yellows and oranges; indanthrene greens; algole greens; indanthrene blues; algole blues; indanthrene grey; indanthrene browns; algole browns; cibanone browns.

The application of the indigoid vat dyes to wool and silk.—Vats suitable for the dyeing of wool and silk are obtained by reduction with sodium hydrosulphite in alkaline (caustic soda) solution. Bright reds of excellent fastness are obtained with these dyes, and they are used in conjunction with indigo for producing bright purplish blues. Separate vats are preferable for the indigo blue and the red dye, since the best conditions of dyeing do not coincide in the two cases.

The application of indigoid vat dyes to cotton.

—Vegetable fibres are readily dyed with these dyes from a hydrosulphite vat, or alternatively they may be dyed from a sodium sulphide bath, as used for the sulphide dyestuffs. They may be mixed with most sulphide dyes and dyed from the same vat.

The application of the anthracene vat dyes.—This group of dyes are also applied in the hydrosulphite vat, but usually require such a strongly caustic solution that their application to wool and silk is not practicable.

By use of the vat dyes, it is now possible to produce a great variety of colours on cotton which are extremely fast to light, washing, and other influences. The high cost of these dyes at present somewhat limits their application.

Indophenol is a vat dye of different type, being obtained by the action of nitroso-dimethyl aniline on α-naphthol. On reduction, it is converted into *indophenol white*, a body sufficiently stable to be sold commercially. On oxidation with chromic acid, indophenol white is reconverted into indophenol blue.

Indophenol has been employed in conjunction with, or as a substitute for indigo, but has the defect of being readily affected by acids.

Tyrian purple.—As the result of an extremely interesting investigation, P. Friedländer has shown (Ber. 1909, 765) that this ancient dyestuff is identical with one of the dibrom-indigotins. Tyrian purple, as described by Pliny, was obtained from various species of the mollusc *murex*, and from 12,000 of the species *M. brandaris* Friedländer obtained 1·4 grams of the colouring matter.

Under the law of the ancient Romans, the use of Tyrian purple was confined to royalty, and the method of its production was a lost art for many centuries. At the beginning of the 18th century, it was investigated by Reaumur (Mém. de l'Acad. Royale des Sciences, 1711), but it never again assumed any importance as a dye-stuff.

CLASS VIII.—**The ingrain dyes.** The term *ingrain dye* may be applied to designate those colouring matters other than mordant dyes which are produced from their constituent bodies *upon the fibre*. Three sub-groups may be distinguished: (*a*) *aniline black*; (*b*) *the insoluble azo- dyes*; and (*c*) *the metallic dyes*.

(*a*) *Aniline black.*—This term is applied to the insoluble black pigment which is produced by the oxidation of aniline in acid solution. In 1834 Runge noticed that a blue-black compound was produced by oxidising aniline with chromic acid, but Wilm, in 1860, first described the formation of the product on the cotton fibre. The first successful aniline black was patented by Lightfoot, in 1863, who used potassium chlorate and cupric chloride as oxidising agents, and the black proved to be of such excellent fastness that innumerable modifications of the process have since been proposed, and the literature of the subject is very extensive.

Numerous oxidising agents have been employed in the production of aniline black, *e.g.* chlorates, chromates, salts of copper, vanadium, tungsten, cerium, &c. Aniline black may also be produced by electrolytic (Goppelsröder, Jahresber. 1876, 702) or by atmospheric (Green, J. Soc. Dyers, 1908, 231) oxidation.

Pure aniline on oxidation yields a blue-black, the homologues and allied compounds giving somewhat different shades; *e.g.* orthotoluidine produces a brownish-black, paraphenylene diamine a deep black, and para-aminodiphenylamine (diphenyl base) a greenish black. The oxidation of α-naphthylamine on the fibre results in the formation of *naphthylamine violet*, but this colour is not of much importance.

The composition of aniline black has been the subject of much investigation (*see* Armand Müller, Chem. Zentr. 1871, 288; Goppelsröder, Jahresber. 1876, 702; Nietski, Ber. 1878, 1094; Caro, Verhandt. d. Ges. Deutscher Naturforchen u. Arzte, 1896, 119; Willstätter and Moore, Ber. 1907, 2665; Marsden, J. Soc. Dyers, 1908, 9; Willstätter and Moore, Ber. 1909, 4118; Green and Woodhead, Chem. Soc. Trans. 1910, 223).

Three chief and successive products of the oxidation of aniline may be distinguished—*emeraldine, nigraniline*, and *ungreenable black*.

Emeraldine is produced by the limited oxidation of aniline, several residues linking up to form a chain of 4 molecules (Willstätter and Moore) or a chain or ring of 8 molecules (A. G. Green). The aniline residues are in all probability linked by nitrogen atoms in para- position, since para- compounds only have been obtained on oxidation or reduction.

Emeraldine is a greyish-green body which is always formed during the early stages of the production of aniline black. By the action of oxidising agents, it is converted into nigraniline and by the action of reducing agents it forms first proto-emeraldine by addition of two atoms, and then leuco-emeraldine by addition of four atoms of hydrogen (Green, Chem. Soc. Trans. 1910, 223). More powerful reducing agents split the molecule and produce amino- and para-diamino-compounds.

Nigraniline, the second oxidation product of aniline, appears to contain eight aniline residues, and is produced either by removal of two hydrogen atoms from the emeraldine molecule (Green) or by polymerisation with loss of hydrogen (Willstätter and Moore).

Nigraniline or aniline black is a violet-black body which is unaffected by alkalis, but which is turned green by mild reducing agents (sulphurous acid), owing to its reconversion into emeraldine. Dilute mineral acid also brings about indirectly the production of emeraldine from nigraniline. Oxidation of a portion of the latter substance probably takes place at the expense of the reduction of other molecules, since both quinone and emeraldine are formed in the reaction.

Ungreenable black, the final product in the technical formation of aniline black, is produced by the further oxidation of nigraniline in presence of aniline. It is a very stable body, and is not readily attacked by acids, alkalis, oxidising or reducing agents. Powerful oxidising agents, however, convert it almost quantitatively into quinone, and powerful reducing agents into a brown leuco- compound which is reoxidised to the original black on exposure to air. The presence of free aniline is essential to the production of ungreenable black, which suggests that it is a condensation product of emeraldine and aniline.

Technical production of aniline black.—Of the large number of modifications of Lightfoot's

original process which have been suggested, very few have withstood the test of practical experience. The following technical methods may be distinguished: (1) *dyed blacks*; (2) *aged blacks*; (3) *steam blacks*.

(1) *Dyed blacks*, also known as *one-bath blacks*, are used for the dyeing of cotton yarn, which is often previously dyed in a sulphide black vat. The ingredients used are aniline (12 lbs.), hydrochloric acid (18 lbs.), sulphuric acid (24 lbs.), and sodium dichromate (24 lbs.), in 40 gallons of water. The use of hydrochloric acid alone produces a bluish-black, and sulphuric acid alone a reddish-black, the mixed acids yielding a jet black.

The yarn is worked in the solution while slowly heating to the boiling-point, and the bronzy black thus produced is steamed to convert it into a good black which is ungreenable. This process does not tender the cotton. Many modifications of the process are used.

(2) *Aged blacks* are obtained by padding (saturating) the cotton with a solution containing aniline salt, some oxidising agent (sodium chlorate) and an oxygen carrier (copper sulphate, or vanadium chloride), after which the fabric is dried and 'aged,' or the colour developed, by passing through an ageing chamber in which a moist atmosphere and a temperature of about 45° are maintained. The padded cotton has a green colour (emeraldine) which turns black (nigraniline) during ageing. The final change to ungreenable black is brought about by working the fabric in a solution of sodium dichromate.

Copper aged blacks are very largely produced on cotton piece goods by a process which differs only in detail from Lightfoot's original process.

Vanadium blacks are chiefly used in calico printing. Lightfoot (Bull. Soc. Ind. de Mulhouse, 1871, 285) first noticed the special efficiency of vanadium salts as oxygen carriers in the production of aniline black, and Witz (Bull. Soc. Ind. de Rouen, 1876, 310) showed that 1 part of vanadium chloride was sufficient to convert 40,000 parts aniline into aniline black.

Aged blacks are liable to tender the cotton unless their production is very carefully controlled.

Air oxidation black.—A. G. Green (J. Soc. Dyers, 1909, 191) has introduced an aniline black process in which atmospheric oxygen is the oxidising agent; some carrier such as cuprous chloride being present. The mineral acid usually employed is also replaced by formic acid, and by these modifications the liability to tendering of the fibre is greatly reduced.

The process is based on the fact that aniline oxidises much more readily in presence of a small quantity of a paradiamine or a para-aminophenol.

After padding, the goods are dried, aged, and chromed as in the case of the ordinary aged black.

(3) *Steam blacks* are more costly but safer than aged blacks as regards tendering of the fibre. They are produced by padding with an aniline solution which contains sodium chlorate as oxidising agent, and sodium ferrocyanide as oxygen carrier. After padding, the goods are dried, steamed, and chromed. Lightfoot's original steam black only differed in that it contained potassium ferricyanide in place of the less expensive sodium chlorate and ferrocyanide.

Aniline black, when successfully dyed on cotton, is the fastest and most intense black which it is possible to produce. Its chief drawbacks are the tendency to turn green and the liability to tendering of the fibre, unless great experience and close supervision are exercised.

Application of aniline black to wool and silk.—The animal fibres are rarely dyed aniline black. The black may be produced on silk by the same methods as on cotton, but the process is chiefly confined to the silk-cotton union material used for umbrella cloth.

Aniline black does not readily develop on wool, but if the wool is previously chlorinated (Lightfoot) or boiled with a mineral acid (Bethmann, Eng. Pat. 1901, 21236), the aged black may be produced. It is rarely met with.

(*b*) *The insoluble azo- dyes.*—The sulphonated azo- dyes which are so largely used in the dyeing of wool and silk have little or no affinity for cotton. Azo- compounds are, however, produced on cotton by impregnating the fibre with one of the constituents, and then passing it into a solution of the necessary combining body. The non-sulphonated compounds are used in this process, and the insoluble dyes thus obtained are, in many cases, useful colours.

The constituent parts of an azo- dye are (*a*) a phenol or amine, and (*b*) a diazotised base; and the process (introduced by Holliday, in 1880) consists in saturating the cotton with an alkaline solution of a phenol, drying, and then developing in a solution of the diazotised base.

In calico printing (rarely in dyeing) the fibre may be impregnated with a paste containing the whole of the colour ingredients, and the colour developed by steaming.

Substances employed in the process: *Phenols.* The only phenol practically employed in the padding operation is β-naphthol. Amines are not used.

Aromatic bases.—The following list gives the principal bases employed and the colours they produce when combined with β-naphthol:—

Base	Colour produced with β-naphthol
Aniline	Orange yellow
Paranitraniline	Red (with copper, brown)
Paratoluidine	Yellow orange
Nitroparatoluidine	Orange
Xylidine	Red
Cumidine	Bluish-scarlet
Phenetidine	Scarlet
α-Naphthylamine	Blue shade of claret red
Aminoazobenzene	Crimson
Benzidine	Purplish-brown
Tolidine	Reddish-brown
Dianisidine	Blue (with copper)
Azo-black base	Black

Padding or grounding.—The intensity of the ultimate colour depends entirely upon the concentration of the padding solution, which, for a shade of medium strength may contain, per litre, 25 grams β-naphthol, 45 grams sodium hydroxide solution 36°Tw., and 75 grams Turkey-red oil. Cotton is evenly saturated in the cold with this solution, then dried at a low temperature and developed.

The developing process.—The most important dye produced by this process is *paranitraniline red*, which is dyed on a very large scale and used

as a substitute for Turkey red. The diazo-solution is prepared as follows: Stir to a paste 10 lbs. paranitraniline with 2 gallons water; then add 2 gallons hydrochloric acid (35°Tw.) and 6 gallons water. After mixing well, add 5½ lbs. sodium nitrite dissolved in 2 gallons water. Dilute to 200 gallons, and add sodium acetate to neutralise the excess of hydrochloric acid. The colour is produced instantaneously on passing the padded cotton into this solution, the cotton being subsequently washed, dried, and soaped.

Various stable forms of the diazotised base appear under the names azophor red, nitrazol, and nitrosamine red.

Azo-oranges, yellows, crimsons, claret-reds, &c., are obtained in a similar manner by the use of the various bases given in the above table.

Azo-browns are produced by adding an alkaline solution of copper to the β-naphthol prepare, and developing with paranitraniline or β-naphthylamine.

Azo-blues are obtained by padding with β-naphthol, developing with dianisidine, and subsequently treating with cupric chloride and chromic acid.

(*c*) *The metallic dyes*: *Iron buff and Nankin yellow.*—These two colours, which differ only in depth of shade, are produced by precipitating hydrated ferric oxide on the fibre. They are dyed chiefly on cotton, and produce yellow to light-brown colours which are fast to light, washing, or alkalis, but are readily attacked by acids. The cotton is padded in a solution of a ferrous or ferric salt, and then passed into an alkaline solution. If the cotton is previously mordanted with tannin, more regular shades are produced, the black tannate of iron being subsequently destroyed by a treatment with sodium peroxide (Knecht) or other oxidising agent. Iron buff is only produced on wool or silk as an intermediate product in dyeing Prussian blue.

Manganese bronze.—This colour is produced on cotton by precipitating manganous hydroxide on the fibre, and oxidising this to the brown manganic peroxide.

Chrome yellow is produced on cotton by impregnating with a solution of lead acetate, drying, and passing into a solution of potassium dichromate.

Chrome orange.—This compound is a mixture of normal lead chromate (chrome yellow) and basic chromate.' It is obtained by treating cotton dyed chrome yellow with lime water.

Prussian blue is produced on cotton by first dyeing an iron buff, and then passing into an acid solution of potassium ferrocyanide. This colour is extremely fast to light, but is sensitive to alkalis. It is produced on silk in a similar manner as a constituent in dyeing the fibre black. Prussian blue is little used on wool, but is readily produced either by a process analogous to the above, or by making use of the fact that when heated in acid solution with wool, the prussiates undergo decomposition with formation of Prussian blue.

Colouring Matters used in Dyeing.

Natural dyestuffs: *Indigo.*—There are two distinct methods of applying indigo in dyeing, and the most important, the vat method, has already been described (*v. Vat dyes*, p. 293). Indigo may also be used as an acid dyestuff by converting it into a sulphonic acid. The sulphonic acid is known as indigo carmine or indigo extract. It dyes a brighter blue shade than vat indigo, but it is much less fast to light and washing. It is largely used on wool and silk, but is inapplicable to cotton.

Logwood is a mordant dyestuff used for all fibres. On *wool* it is largely employed for producing blacks, and in conjunction with other dyestuffs for browns, olives, greys, &c.

Potassium or sodium dichromate, the usual mordant, but a single-bath logwood black may be produced by using a mixture of logwood, ferrous sulphate, and oxalic acid. Logwood is now chiefly employed in the form of unoxidised (for cotton) or oxidised (for wool) extract. On *silk* and *cotton*, logwood is only used for black dyeing.

Brazilwood, peachwood, and *Limawood* constitute the class of soluble red woods. They are now very little employed, the colours they produce being fugitive to light. They produce reddish-browns with chromium, and purples with iron mordants.

Camwood, barwood, and sanderswood are known as the insoluble red woods. If wool is boiled with the ground wood, it acquires a reddish-brown colour, which is still employed as a 'bottom' for indigo vat blue. They are, however, mordant dyestuffs, producing brownish reds with chrome mordant.

Madder.—This dyestuff, once of great importance, has now been almost entirely superseded by synthetic alizarin. It is still used to a limited extent in the dyeing of wool felt, since it penetrates through the material more readily than alizarin. With chromium mordant it gives a reddish-brown; with aluminium a red, and with iron a purple shade. The use of madder in the woad vat has already been referred to (*v. Vat dyes*). This dyestuff is now not used on cotton or silk.

Cochineal.—The use of this valuable dyestuff in dyeing is now confined to the production of scarlet shades on woollen cloth, for which purpose considerable quantities are still imported. Stannous chloride is the mordant employed, and the colour is produced by the one-bath method. The aluminium and tin lakes are used as pigments in painting and printing.

Lac-dye may be employed in the same way as cochineal, and gives similar shades. Since the commercial product contains a considerable amount of mineral matter, the ground dyestuff is treated with dilute hydrochloric acid before use.

Cudbear and orchil (or *archil*). These products are essentially the same dyestuff, the former in the solid and the latter in the condition of paste. It is one of the few natural colouring matters which dye wool without a mordant. Wool and silk may be dyed in a neutral, slightly acid, or slightly alkaline, solution. It produces full, rich crimsons, and is still used to a considerable extent. The colouring matter is not applicable to cotton.

Safflower was formerly much used in dyeing bright pinks upon cotton, but is now obsolete as a dyestuff.

Annatto produces orange shades on silk without a mordant: it is applied in a hot soap-

bath. Annatto is still used in colouring cheese and butter.

Weld.—This mordant dyestuff produces pure yellows in conjunction with aluminium mordant. When used as a 'topping' for indigo vat blue, a special shade of green, known as 'carriage green,' is obtained.

Fustic is the most important of the natural yellow dyewoods, and is still employed in conjunction with chrome mordant on wool as the yellow constituent in compound browns, olives, greys, &c. It is chiefly used in the form of fustic extract.

Quercitron bark and flavin are also natural yellow mordant dyes, producing somewhat brighter shades than fustic, but now obsolete.

Persian berries.—This mordant dyestuff is employed by the calico printer for producing bright orange shades with tin mordant.

Turmeric is the only representative of the natural colouring matters which acts as a direct dye towards cotton, silk, and wool. It produces yellow shades, which are brighter if dyed in a bath acidified with alum.

Catechu, cutch, and gambier.—These dyestuffs are still largely employed in cotton dyeing. The cotton is steeped in a strong solution of the dye, and attracts the colouring matter. The cotton is then passed into a boiling solution of potassium dichromate, which, by oxidation, produces insoluble brown japonic acid upon the fibre. A little copper sulphate is frequently added to the catechu bath, whereby fuller and faster shades are produced.

Silk is dyed in a similar manner in the production of weighted blacks, the chromium, fixed during the oxidising process, subsequently acting as a mordant for logwood.

Other natural dyestuffs.—Colouring matters are very widely distributed in the vegetable kingdom, and all countries where the textile arts have attained any great development (notably India, Persia, and Japan) had until recently each its own series of indigenous products which were used as dyestuffs. In Donegal, Sutherland, and other localities, the homespun tweeds, &c., are still largely dyed by means of the various lichens, roots, barks, nuts, &c. found in the neighbourhood.

Synthetic dyestuffs. The number of individual synthetic dyestuffs now at the dyer's disposal is very large, and includes dyes belonging to all groups and yielding all possible hues. There is infinite variety in the characteristics of the various artificial dyes, and in most cases it is not difficult to match a given shade or to comply with given conditions as regards properties. Being, therefore, more convenient to use, and in very many cases cheaper and faster than the natural dyestuffs, the latter are being gradually superseded.

The dyeing properties and the characteristics of the dyed colours depend chiefly upon the chemical groups to which the dyes belong, but, as indicated in the section dealing with the classification of dyes, the chemical groups do not coincide with groups based on the method of application (*v. Classification of colouring matters*).

(1) *Nitroso colouring matters.* This class includes fast-green or dark-green and naphthol-green. In conjunction with iron mordants, both these dyestuffs give olive-green colours remarkable for their fastness to light.

Cotton is dyed with dark-green by mordanting with iron, and dyeing in a neutral bath. Wool is mordanted with ferrous sulphate and oxalic acid, and dyed in a neutral bath. Silk is dyed in a similar manner.

Naphthol green which contains iron is only applicable to the animal fibres. Wool is dyed with the addition of sulphuric acid.

(2) *Nitro-colouring matters.*—The important members of this class are: picric acid, Victoria orange, aurantia, palatine orange, naphthaline yellow, naphthol yellow. These colouring matters are only applicable to the animal fibres, which are dyed in a bath slightly acidified with sulphuric acid. The colours they yield are not fast to light. Picric acid yellow is remarkable for its extreme freedom from any trace of orange. On exposure to light it rapidly becomes orange.

(3) *The azo- group.*—These may be divided into monazo-, disazo-, trisazo-, and tetrakisazo- dyes, according to the number of azo- groups they contain. They may be further classified into aminoazo- (NH_2) and oxyazo- (OH) dyes, and into other subdivisions based upon the state of combination of the azo- group. A few of the azo- colours are basic dyes; a large number of the acid dyes belong to this group, and practically the whole of the direct dyes. The azo-dyes vary greatly in their degree of fastness to light, and in other properties.

(4) *The di- and tri-phenylmethane group.*—This group includes most of the basic dyes, such as auramine, magenta, methyl violet, malachite green, &c. These bodies, when sulphonated, form acid dyes, and therefore such dyestuffs as acid magenta, guinea green, &c., and also patent blue, Victoria blue, fall under this group. As a class, these dyestuffs are fugitive to light.

(5) *The oxyketone group.*—This group includes most of the artificial mordant dyes; *e.g.* the alizarin reds, yellows, blues, browns, &c. Most of the dyestuffs of this group are extremely fast to light and other influences, which renders them of the greatest importance.

(6) *The pyronine group.*—This includes (1) the pyronines proper, a small class of basic dyes, of which pyronine red is an example; (2) the much more important group of the phthaleins. The latter includes both basic and acid rhodamines, the eosins and the mordant dyestuffs gallein and cœrulein.

(7) *The acridine group.*—This includes a few basic dyestuffs of which the chief is acridine orange.

(8 and 9) *The oxazine and thiazine group.*—This group also includes both acid (thiocarmine), basic (methylene blue), and mordant dyes (gallocyanin).

(10) *The azine group* includes the valuable basic dyes the safranines, and the basic and acid indulines and nigrosines.

The dyeing of mixed fabrics of cotton and wool may be carried out by selecting those colouring matters for which both fibres have an attraction, *e.g.* the benzidine dyes, &c., or by first dyeing the wool in the usual manner with an acid colouring matter, then mordanting the cotton with tannic acid and tartar emetic or stannic chloride, and dyeing in the cold with

a basic colouring matter. The so-called "cross-dyeing" process is carried out by first dyeing the cotton warp, then weaving with a wool weft and dyeing the latter by means of acid dyes. Logwood blacks on union are dyed by first mordanting the cotton in the cold with tannic acid and nitrate of iron, then the wool with a boiling solution of potassium dichromate, and finally dyeing both fibres thus mordanted in a hot decoction of logwood. Mixtures of cotton and silk are dyed by methods similar to those employed for cotton and wool. Fabrics of wool and silk are dyed by methods similar to those usual for wool or silk alone.

When dyeing *compound shades*, the main principle to be observed is to apply simultaneously only such colouring matters as are applicable, when used singly, by methods as similar as possible to each other. Basic and acid colouring matters ought not to be applied together in the same dye-bath, since the one requires a neutral, the other an acid, bath in order to yield their full colouring power. Basic colouring matters, however, may be quite well applied to mordanted cloth along with phenolic colouring matters, since both these classes usually dye in a neutral bath.

It is very irrational to produce compound shades by the application of a mixture of fast and fugitive colours; the best results are obtained by employing colouring matters of about equal fastness to various influences. If this rule is not observed, the dyed colour is liable to change materially in shade under those influences to which it is subsequently submitted, *e.g.* light, washing, &c.

For further information on the subject of dyeing, the following works may be consulted:—

1813. The Philosophy of Permanent Colours. E. Bancroft.

1835–1861. Recherches chimique sur la Teinture. E. Chevreul.

1869. Dictionary of Dyeing and Calico-printing. C. O'Neill.

1874. A Practical Handbook of Dyeing and Calico-printing. W. Crookes.

1876. Dyeing and Calico-printing. F. C. Calvert.

1885. The Dyeing of Textile Fabrics. J. J. Hummel.

1893. La Pratique du Teinturier. Vol. 1, 1893; Vol. 2, 1894; Vol. 3, 1897. J. Garçon.

1901. Dictionary of Dyes, Mordants, and other Compounds used in Dyeing and Calico-printing. C. Rawson, W. M. Gardner, and W. F. Laycock.

1903. Theorie und Praxis der Modernen Färberei. A. Ganswindt.

1904. Systematic Survey of the Organic Colouring Matters. G. Schultz and P. Julius, transl. by A. G. Green.

1905. Synthetic Dyestuffs and Intermediate Products from which they are derived. J. C. Cain and J. F. Thorpe.

1907. Färbereichem. Untersuchungen Anleitung zur Untersuchung und Bewertung der wichtigsten Färberei, Bleicherei, Druckerei, und Appretur-Materialien. 2nd edit. P. Heermann.

Étude sur les Industries du Blanchiment, de la Teinture, de l'Impression. O. Picquet.

1910. A Manual of Dyeing. 2nd edit. E. Knecht, C. Rawson, and R. Lowenthal.

Identification of the Commercial Dyestuffs. Mulliken. W. M. G.

DYESTUFFS, IDENTIFICATION OF, ON FABRICS. The recognition of the particular dyestuff which has been employed in dyeing a fabric is frequently a matter of considerable difficulty. If one dyestuff only has been used, it may be possible to identify it with little trouble, but when, as is often the case, two or more dyes have been employed to produce a given colour, their separation and recognition may become a very complex problem.

In the identification of dyestuffs, the ordinary basis of qualitative analysis is as far as possible made use of, *i.e.* the *group* to which the colouring matter belongs is first determined, and then tests are applied to identify it as an individual substance. There are, however, such a large number of closely related compounds amongst the dyestuffs, many being isomeric, and differing only (*e.g.*) in the position of a sulpho- group, that with the small amount of substance frequently at disposal it is quite impossible to definitely identify a specific commercial product. This is, however, of minor importance.

The recognition of a dyestuff is greatly facilitated by a knowledge of the dyeing properties of the various groups of colouring matters. In a given case this may greatly limit the possibilities. For example, no one with a knowledge of dyeing processes would search for a cochineal scarlet on cotton or a paranitraniline red on wool. The presence or absence of certain metallic bases in the ash of the incinerated material is also a useful indication of the nature of the dyestuff under investigation, and an examination of this point should be made.

What may be termed the 'dyeing groups' of colouring matters do not coincide with the 'chemical groups.' For example, the dyeing group of 'basic' dyes, the members of which are fixed on cotton by means of a tannin mordant, includes members of the triphenyl methane, azine, azo-, acridine, and other chemical groups.

To determine the dyeing group to which a colouring matter present on a fabric belongs, acid and alkaline solvents are used as 'stripping' agents. The following are the general reactions:

ACTION OF 'STRIPPING AGENTS.'

Dyeing group	*Stripping solution*
Mordant dyes	50 c.c. HCl (conc.) per litre
Basic dyes on wool	5 p.c. acetic acid
„ „ on cotton	3 p.c. sodium hydroxide
Acid dyes Direct cotton dyes	3 p.c. ammonia 0·880 s.g. A small piece of mercerised cotton is placed in the solution.

In each case the fabric is boiled for 5 minutes in the solution.

With direct cotton dyes the small piece of white cotton placed in the solution becomes dyed. With acid dyes this does not occur.

The action of the above stripping agents can only be considered as general in regard to a particular group, and many exceptions will be found

in dealing with particular members of the group, *e.g.* some acid dyes are only slightly stripped by boiling in dilute ammonia, and a few of them stain mercerised cotton. Too much reliance must not, therefore, be placed on these stripping reactions.

The most satisfactory group reagents for classifying dyestuffs into the chemical groups are acid or alkaline reducing agents; on the use of which several schemes of identification have been based. These reagents were first proposed by Witt, in 1886, whose scheme was extended by Weingaertner, in 1887; but the systematic development of the scheme of analysis is mainly due to A. G. Green.

The reactions of dyestuffs are considerably influenced by the nature of the fibre upon which they have been fixed, which also determines the particular dyeing process necessary. For example, the basic colours dye wool and silk direct, whereas their fixation on cotton involves the use of a tannin mordant. It is convenient, therefore, to treat separately the identification of dyestuffs on animal and on vegetable fibres.

Identification of dyestuffs on wool.—Tables for the identification of dyestuffs on wool have been published in Hummel's Dyeing of Textile Fabrics; in Knecht, Rawson, and Loewenthal's Manual of Dyeing; in Lehne's Färber Zeitung, and by many other authors; but the most systematic and reliable scheme is that of Green (J. Soc. Dyers, 1905, 236; and 1907, 252). In this scheme, which is now to be described, the dyeing groups are first distinguished by the action of suitable solvents, and then further differentiation is carried out by the use of reducing agents with subsequent reoxidation. The various groups of dyestuffs as dyed on animal fibres, show the following reactions:—

Decolourised by hydrosulphite			Not altered by hydrosulphite	Not decolourised, but changed to brown. Original colour restored by air or persulphate
Colour restored on exposure to air	Colour not restored by air, but restored on oxidation with persulphate	Colour not restored either by air or persulphate		
Azines, oxazines, thiazines, indigo	Triphenylmethane group	Nitro-, nitroso-, and azo- groups	Pyrone and acridine groups. Some members of the oxyketone group.	Most dyestuffs of the oxyketone group

In Green's scheme the following reagents are employed, and must be used of the strength indicated:—

Dilute ammonia (1 : 100).—1 c.c. conc. ammonia; 100 c.c. distilled water.

Aqueous alcoholic ammonia.—1 c.c. conc. ammonia; 50 c.c. strong alcohol or methylated spirit; 50 c.c. water.

Dilute acetic acid (5 p.c.).—5 c.c. glacial acetic acid; 95 c.c. water.

Dilute alcohol (1 : 1).—50 c.c. strong alcohol or methylated spirit; 50 c.c. water.

Dilute hydrochloric acid (1 : 10).—10 c.c. conc. hydrochloric acid; 90 c.c. water.

Caustic soda (10 p.c.).—10 grams solid caustic soda in 100 c.c. of water.

Hydrosulphite sol. A.—A 10 p.c. solution of hydrosulphite NF (M. L. & B.) or 'hyraldite' (Cassella), *i.e.* the formaldehyde compound of sodium hydrosulphite. This solution, which is slightly alkaline, is employed in most cases. In a few other cases, however, in which the reduction is more sluggish (*e.g.* azo- yellows), it is found necessary to employ a slightly acid solution. This is termed

Hydrosulphite sol. B.—Prepared by acidifying 200 c.c. of hydrosulphite A with 1 c.c. of glacial acetic acid.

Persulphate.—A cold saturated solution of potassium persulphate, or a 1 p.c. solution of ammonium persulphate.

Sodium acetate (5 p.c.).—5 grams crystallised sodium acetate; 100 c.c. distilled water.

Procedure.—The reactions are carried out in test-tubes upon pieces of the material about ¾–1 inch square, which are covered with about 1–1½ inches of the reagent. The tests should be carried out exactly as described. In making 'stripping tests,' the degree of stripping is judged by comparing the remaining shade with that of the original pattern. The colour of the stripping solution cannot be relied upon as a guide. In boiling with dilute acetic acid and dilute ammonia, it is found advantageous to repeat the extraction, as a better stripping is thereby obtained, and with acid dyestuffs any staining of the cotton by the first strong extract is removed during the second boil. In testing with dilute ammonia or sodium acetate, the material is placed in a test-tube with a piece of white mercerised cotton cloth, somewhat smaller in size, and boiled for the time prescribed. If the shade is a pale one, the size of the sample should be increased and that of the cotton diminished. The dilute ammonia is replaced by aqueous alcoholic ammonia in the case of the violet and black dyestuffs (Tables III. and VII.), as in these cases the acid dyestuffs are less easily extracted, and the cotton is more liable to be stained by them. In making reduction tests, the sample is boiled for from one-quarter to one minute with the hydrosulphite, then rinsed well under the tap, and allowed to lie on white paper. With most dyestuffs which form air-oxidisable leuco- compounds, the colour returns immediately or in a few minutes, but with others a longer time is required. The reaction is accelerated by exposing the pattern to ammonia

vapour. If the colour does not return, the pattern is boiled with a little water *in* a test-tube, and potassium persulphate is added drop by drop, carefully avoiding an excess. If this also fails to cause any return of colour, the dyestuff is to be regarded as a nitro-, nitroso-, or azo- compound. The depth of the restored colour varies greatly in different cases; with some dyestuffs the colour reappears with nearly its original depth, but with others (probably on account of the greater solubility of their leuco- compounds) only a pale shade may return. Safranine and its azo- derivatives are peculiar in yielding a violet colour on reoxidation of the leuco- compound, this being due to the condensation of the leuco-safranine with the formaldehyde present in the hydrosulphite NF.

The tables (I. to VII., pp. 302-308) give the scheme of analysis.

These tables do not differentiate between closely related individual dyes, for which purpose further tests must be made. At this stage of the investigation it is very desirable to procure small pieces of material dyed with such known colouring matters as the group tests, combined with the colour of the sample, have indicated as probable. Parallel individual tests should then be applied with these and with the sample under examination.

The following series of reagents have been found by W. M. Gardner to be convenient for this purpose. They should be applied in the order given, and are best used as follows :—

Application of cold reagents.—Steep a piece of the material (say) 1 by ½ inch in (say) 5 c.c. of reagent for 5 minutes in a small porcelain dish.

Application of reagents by boiling.—In a test-tube place (say) 10 c.c. of reagent and a piece of material 1 by ½ inch. Boil *gently* for 3 minutes.

Application of nitric acid test.—On a white glazed porcelain plate, spot the material by dipping a glass rod into the acid and then pressing it on to the cloth. Note the changes in colour which occur during the formation of the spot, and re-examine after several hours, noting any further change.

Reagents for identifying individual dyestuffs:

1. Boiling water.
2. 5 p.c. acetic acid, boiling.
3. 3 p.c. ammonia, boiling.
4. 3 p.c. soap, boiling.
5. Boiling alcohol.

Use small pieces of white wool, silk, and cotton along with the dyed sample.

6. Concentrated sulphuric acid, cold.
7. 3 p.c. ammonium persulphate, cold.
8. Bleaching powder solution, 5°Tw., cold.
9. 50 grams $SnCl_2,2H_2O$+100 c.c. HCl. 32°Tw. per litre, cold.
10. 5 c.c. $NaNO_2$ (5 grams. per litre), and 5 c.c. H_2SO_4 (3·5 grams per litre) boiling.
11. Apply test 10 cold, then wash and steep the material in a solution of sodium β-naphtholate 5 grams per litre.
12. Concentrated nitric acid (spot test).

If the sample under examination shows the same reactions as any one of the control samples, with each of the above reagents, its identity may be considered as clearly established.

Knecht (J. Soc. Dyers, 1904, 98) states that titanous chloride possesses advantages over both stannous chloride and sodium hydrosulphite as a test for dyestuffs. The solution is prepared by boiling together 25 c.c. commercial titanous chloride solution (20 p.c.) and 25 c.c. HCl, 32°Tw., and diluting to 1000 c.c. with water.

Identification of Dyestuffs on Cotton.

Green (J. Soc. Dyers, 1907, 252) has worked out an analytical scheme for the detection of dyestuffs on cotton on the same lines as that previously described for wool.

The reagents are as follows :—

1. *Dilute ammonia.*—1 c.c. strong ammonia to 100 c.c. distilled water.
2. *Dilute caustic soda.*—10 grams caustic soda in 100 c.c. water.
3. *Saline caustic soda.*—10 c.c. caustic soda solution (35–40 p.c. NaOH) to 100 c.c. saturated solution of salt.
4. *Formic acid* 90 *p.c.*—Concentrated commercial acid.
5. *Dilute formic acid.*—1 c.c. formic acid (90 p.c.) to 100 c.c. distilled water.
6. *Dilute hydrochloric acid.*—5 c.c. hydrochloric acid (30 p.c.) to 100 c.c. of water.
7. *Soap solution.*—10 grams soap in 300 c.c. of water.
8. *Tannin solution.*—10 grams tannic acid and 10 grams sodium acetate in 100 c.c. of water.
9. *Bleaching powder solution.*—Fresh solution at 5°Tw.
10. *Hydrosulphite A* (same as for wool).—10 p.c. solution of hydrosulphite NF or of hyraldite, or a 5 p.c. solution of hydrosulphite NF conc., or of rongalite (formaldehyde sodium sulphoxylate).
11. *Hydrosulphite B* (same as for wool).—The preceding solution slightly acidified by addition of 1 c.c. glacial acetic acid to 200 c.c. of solution.
12. *Hydrosulphite X.*—Dissolve 50 grams of rongalite or hydrosulphite NF conc. in 125 c.c. of hot water. Grind 1 gram of anthraquinone (precipitated, not sublimed) to a fine powder, and reduce to a smooth paste with a little of the rongalite solution. Add this paste to the remaining solution, and heat the whole for 1 or 2 minutes at about 90°. Then dilute with cold water to 500 c.c., and, after standing until cold, add 1½ c.c. of glacial acetic acid. Keep in a well-stoppered bottle with greased stopper. The reagent should be tested occasionally by trying its effect on cotton dyed with α-naphthylamine bordeaux, which should be fully discharged after boiling for 1 or 2 minutes. The anthraquinone may be replaced by β-oxyanthraquinone, which can be employed in the same way or previously dissolved in a little alcohol before it is added to the hydrosulphite. It has the advantage of giving a clearer solution, but is not so generally available.
13. *Persulphate solution.*—A cold saturated solution of potassium persulphate, or a 2 p.c. solution of ammonium persulphate.
14. *Acid stannous chloride.*—100 grams stannous chloride to 100 c.c. hydrochloric acid (30 p.c.) and 50 c.c. water. In testing for sulphide colours, this reagent may be replaced with advantage by a strong solution of titanous chloride.

Procedure: *General.*—All the reactions are performed in test-tubes, with pieces of material about ½–¾ of an inch square, which are covered to the depth of from 1½ to 2 inches with the reagent. The degree of stripping is judged by comparing the remaining shade with that of the original pattern; the colour of the stripping solution cannot be relied upon as a guide. In testing the colours of calico prints, the separate colours should be cut out and the reactions tried upon them separately. With cotton and wool, or cotton and silk unions, the weft is separated from the cotton warp, and both submitted to examination. Doubt may frequently exist as to how a particular shade should be classified, whether, for instance, a reddish-blue is to be regarded as a blue or a violet. In such cases the tables referring to both shades should be employed; but since the same general scheme is adopted throughout the tables, this can scarcely give rise to confusion. The same remark applies to possible mixtures; thus in examining a certain green shade, both the yellow and the blue tables may have to be used.

It is obvious that in many instances the analytical procedure may be greatly simplified by exclusion of dyestuffs the presence of which is rendered improbable or impossible by the special circumstances of the case, *e.g.* by the material, shade, or mode of application of the colour.

Stripping test.—A few of the direct dyestuffs are partially stripped by dilute ammonia, and may thus give rise to the impression that they are acid colours. To avoid this error, it is advisable to add a small piece of white cotton when carrying out the test. With an acid dyestuff the cotton is either not tinted or becomes white on boiling a second time with dilute ammonia.

Transference of basic dyes to wool.—The tannin mordant is first removed, as in testing for a basic colour, by boiling the pattern for half a minute with saline caustic soda. It is then well washed to remove all alkali, and is boiled with a piece of white wool (half the size of the cotton or less) in a little water for 1 or 2 minutes. In most cases the dye base will leave the cotton almost entirely, and dye the wool a full shade. If the colour does not develop on the wool, one or two drops of dilute formic acid (1 : 100) may be added. In the case of a few dyestuffs which are more difficult to strip (*e.g.* basic greys), it is necessary to extract the colour with dilute hydrochloric acid (1 : 20), carefully neutralising the extract with ammonia before adding the wool.

Tannin test for basic dyes.—Add a few drops of tannin solution to the formic acid extract. Shake well, and if the precipitate does not form at once, allow to stand a few minutes. Some colouring matters such as the rhodamines, gallocyanines, and chrome colours of the rosaniline series (which contain carboxyl- or hydroxyl- groups in addition to basic groups) only precipitate slowly, and the precipitate, being more finely divided, is sometimes difficult to see.

Bleeding test for direct dyestuffs.—In testing for direct dyestuffs by the bleeding test, the sample is placed in a test-tube together with a smaller piece of white mercerised cotton cloth, and boiled with soap solution for about a minute. The soap solution may be replaced by a 5 p.c. solution of sodium carbonate.

Lead acetate test for sulphide dyes.—The sample is first boiled for two minutes with a 10 p.c. solution of sodium hydroxide to remove any adventitious sulphur compounds. It is then well washed and just covered with acid stannous chloride solution. The mouth of the test tube is closed by a cap of filter paper closely wrapped round it, into the centre of which is placed, by means of a glass rod, one drop of lead acetate solution. The contents of the test-tube are slowly heated to the boiling-point, when a blackish-brown stain of lead sulphide appears if a sulphide colour is present. The brown spot will again disappear on continued boiling on account of the decomposition of the lead sulphide by the hydrochloric acid evolved. It is important to pay special attention to the cleanliness of the test-tubes employed for this test, as tubes which have been previously used for hydrosulphite reductions acquire a thin invisible deposit of sulphur upon their walls, which, on boiling with stannous chloride, gives rise to hydrogen sulphide, and thus may lead to error.

Reduction and reoxidation tests.—The reduction with hydrosulphite X is carried out by boiling the sample with the reagent for from a minute to a minute and a half. The azines, thiazines, oxazines, &c., and most of the azo-dyestuffs are fully reduced in about half a minute, but the insoluble azo- colours and some direct dyestuffs require longer boiling to complete their reduction. In testing the reoxidisability by air, the reduced sample may be exposed to the fumes of ammonia, which in many cases accelerates oxidation.

The analytical tables worked out by Green for the identification of dyestuffs on cotton, are given on pp. 309-315, Tables VIII. to XIV.

S. T. Mulliken (Identification of the Commercial Dyestuffs, 1910) has published a systematic scheme of analysis, primarily intended for the examination of the dyestuffs in substance. The tables give the reactions of 1475 distinct dyestuffs, and are of great service in the identification of dyes on the fibre.

Spectroscopic examination of dyestuffs.—The absorption spectra of dyestuffs may be used as an aid to their identification. In the second edition of Vogel's 'Practische Spectralanalyse irdischer Stoffe' (1889), charts were given of the absorption bands of various dyestuff solutions. This work was greatly extended in 'Formánek's Spectralanalytischer Nachweis Künstlicher organischen Farbstoffe' (1900), which contains a systematic scheme for the spectroscopic identification of upward of 350 distinct dyestuffs. In a later publication (1905) entitled 'Qualitative Spectralanalyse anorganischen und organischen Körper,' Formánek has extended his data to include the natural colouring matters, and, in conjunction with E. Grandmougin, has republished his tables as 'Untersuchung und Nachweis organischen Farbstoffe auf spectroscopischen Wege.'

The value of spectroscopic tests for the identification of dyestuffs on the fibre is limited to those dyestuffs which can be removed without change by suitable solvents.

Spectroscopic examination of dyed fibres has not yielded useful results. W. M. G.

RECOGNITION OF DYES ON WOOL OR SILK.

TABLE I.—YELLOW AND ORANGE COLOURS.

Boil twice for one minute with 5 p.c. acetic acid

Much colour is stripped :—Basic dyestuff. Boil with hydrosulphite B						
Not decolourised or only very slightly. Treat fibre with conc. H_2SO_4	Colourless solution. Boil with dilute HCl (1 : 10)	Fibre and solution pale yellow			3	Thioflavine T.
		Completely decolourised			2	Auramine O and G.
	Green fluorescent solution :—Acridine group				1	Phosphine, benzoflavine, rheonine, patent phosphine, acridine yellow, acridine orange, &c.
Little or no colour is stripped :—Acid, Direct, or Mordant dyestuff. Boil twice for one minute with dilute ammonia (1 : 100) and a piece of white cotton. Keep the ammoniacal extract						
Much colour is stripped, but cotton remains white :—Acid dyestuff. Boil with hydrosulphite B	Decolourised, and colour does not return on exposure to air or upon oxidation with persulphate :—Azo- group or Nitro- group. Add conc. HCl to the ammoniacal extract	Becomes violet or violet-red			9	Metanil yellow, orange IV.
		Becomes red			8	Fast yellow, Indian yellow, azoflavine, curcumeine, orange II.
		Becomes colourless			7	Naphthol yellow S, martius yellow.
		No change of colour			6	Tartrazine, oranges G, 2G, R, &c.
	Colour is not affected :—Quinoline or Pyrone group				5	Quinoline yellow, uranine, eosin orange.
Decolourised. Colour is not restored by air or by persulphate :—Azo-group					4	Chrysoidine, tannin orange, new phosphine, Janus yellow.
Little or no colour is stripped. The cotton remains white (Mordant dyestuff) or is tinted (Direct dyestuff). Boil with 5 p.c. sodium acetate and white cotton for two or three minutes	The cotton is stained :—Direct dyestuff. Boil with hydrosulphite B	Not affected :—Thiazol- group			10	Thioflavine S, chromine, chloramine yellow, chlorophenine, diamine fast yellow B and FF, thiazol yellow, clayton yellow, &c. Also turmeric.
		Decolourised. Colour restored by exposure to air or more quickly by persulphate :—Stilbene group			11	Curcumine S, direct yellows, mikado yellows and oranges, stilbene yellows, naphthamine yellows, diphenyl citronine, &c.
		Decolourised. Colour not restored by air or by persulphate:—Azo-group			12	Chrysophenine yellow, chrysamine, carbazol yellow, cresotine yellow, diamine yellows, benzo, Congo, or diamine oranges, toluylene yellow and orange, pluto orange, dianil orange, pyramine orange, &c.
	The cotton remains white :—Mordant dyestuff. (Confirm by testing ash for metallic mordants.) Boil with hydrosulphite B	Not affected :—Flavone and Ketone group			13	Fustic, quercitron, weld,[1] alizarin yellow A, galloflavine, &c.
		Colour changed to yellowish-brown :—Alizarin group			14	Alizarin orange.
		Decolourised and colour not restored by air or persulphate :—Azo-group			15	Alizarin yellows G and R, anthracene yellow C, flavazol, diamond flavine, chrome orange, &c.

[1] Weld is partly discharged by acetic acid, though the extract remains colourless.

RECOGNITION OF DYES ON WOOL OR SILK.

TABLE II.—RED COLOURS.

Boil twice for one minute with 5 p.c. acetic acid

The colour is stripped:—Basic dyestuff or Soluble red woods. Boil with dilute alcohol (1 : 1) twice for one minute	Little or no colour is stripped:—Acid, Direct, or Mordant dyestuffs. Boil twice for one minute with dilute ammonia (1 : 100) and a small piece of white cotton. Keep the ammoniacal extract	Much colour is stripped, but cotton remains white:—Acid dyestuff. Boil with hydrosulphite A	Colour of wool not altered:—Pyrone group. Acidify the ammoniacal extract				1	Basic dyestuff of pyrone group, *e.g.* rhodamines, irisamine, rhodines, anisolines, pyronines.
							2	Basic dyestuff of azine group, *e.g.* safranine, induline scarlet, rhoduline red, rhoduline pink, &c.
							3	Basic dyestuff of triphenylmethane group, *e.g.* magenta, fuchsine, isorubine, cerise, new magenta, &c.
							4	Basic azo- dyestuff, *e.g.* Janus red.
							5	Soluble red woods, *e.g.* brazilwood, limawood, peachwood, &c.
							6	Eosin, phloxin, erythrosin, safrosin, rose bengal, &c.
							7	An acid eosin, or acid rhodamin, *e.g.* fast acid eosin, fast acid phloxin, acid rhodamin, acid rosamin, &c.
							8	Azocarmine or rosinduline.
							9	Acid magenta.
							10	Chromotropes, azofuchsine, &c.
								Biebrich scarlet, &c.
								Crocein scarlet, fast red B, &c.
								Crystal scarlet, fast red A, &c.
								Xylidine or Palatine scarlet.
							11	Cochineal scarlet.
							12	Archil or cudbear.
							13	Anthracene red.
								Hessian purple.
								Diamine fast red.
								Diamine scarlet.
								Erica, geranines.
								Dianthine or rosophenine.
							14	Cochineal crimson.
							15	Alizarin reds.
							16	Insoluble red woods, *e.g.* camwood or barwood.
							17	A mordant azo- colour.

Unaffected. Al or Cr are present in ash. Boiling with dilute ammonia renders the colour much bluer

Much of the colour is stripped:—Basic dyestuff. Boil with hydrosulphite A

Decolourised. Colour is not restored either by air or by persulphate

Decolourised. Colour does not return on exposure to air, but is restored by persulphate

Decolourised. Colour returns quickly on exposure to air

Colour not affected

Precipitation and disappearance of fluorescence

No ppt. and flourescence remains

Decolourised. Colour returns on exposure to air :—Azine group

Decolourised. Colour does not return on exposure to air, but is restored by persulphate. :—Triphenylmethane group

Decolourised. Colour not restored either on exposure to air or on oxidation with persulphate :—Azo- group. Boil with dilute dichromate

Changes to dark maroon or violet black

Evaporate ammoniacal extract and dissolve in conc. H_2SO_4

Green solution

Blue solution

Violet solution

Red solution

Colour unaffected.

Some of the colour is stripped and the wool becomes much bluer. Boil with hydrosulphite A

Decolourised. Colour is quickly restored on exposure to air

Colour slowly changed to deep yellow. Original colour not restored on exposure to air

Little or no colour is stripped. The cotton remains white (Mordant dyestuffs), or is stained (Direct dyestuffs). Boil with 5 p.c. sodium acetate and white cotton for 2 or 3 minutes

The cotton is stained :—Direct dyestuff. Test ash for chromium

Chromium is absent. Treat fibre with conc. sulphuric acid

Greenish-blue solution

Blue solution

Violet solution

Violet-red solution

Crimson-red solution

Cr is present. Solution in conc. H_2SO_4 is red

The cotton remains white :—Mordant dyestuff. (Confirm by testing ash for metallic mordants.) Boil with hydrosulphite A

Decolourised. Colour is not restored by persulphate. Cr in ash

Decolourised. Colour is restored by persulphate. Al in ash

Colour slowly changed to yellow or orange. Al in ash

Colour not affected. Al in ash

RECOGNITION OF DYES ON WOOL OR SILK.

TABLE III.—PURPLE AND VIOLET COLOURS.

Boil twice for one minute with 5 p.c. acetic acid	The colour is not stripped :—Acid, Direct, and Mordant dyestuffs. Boil twice for one minute with dilute ammonia and white cotton	Little or no colour is stripped. The cotton remains white (Mordant dyestuffs) or is tinted (Direct dyestuffs). Boil with sodium acetate and white cotton for two or three minutes	The cotton remains white :—Mordant colour. (Confirm by testing for metallic mordants in ash.) Boil with hydrosulphite A						
				Decolourised. Colour is not restored either by exposure to air or by oxidation with persulphate :—Azo- group				15	A mordant azo- colour.
				Decolourised. Colour does not return on exposure to air, but is restored by persulphate :—Triphenyl-methane group				14	Chrome violet.
				Decolourised. Colour returns on exposure to air :—Oxazine group				13	Gallocyanine, prune, celestine blue, &c.
				Colour changed to brown :—Alizarin group. Boil with dilute HCl	Fibre and solution red or reddish-brown			12	Alizarin bordeaux.
					Fibre and solution yellow			11	Alizarin on Fe [1] or Cr.
				Colour not altered :—Pyrone group				10	Gallein.
			The cotton is stained :—Direct dyestuffs					9	Hessian violet, diamine violet, oxamine violet, benzo fast violet, Columbia violet, oxydiamine violet, chlorantine violet, &c.
		Much colour is stripped, but cotton remains white :—Acid dyestuffs. Boil with hydrosulphite A	Decolourised. The colour is not restored either by exposure to air or by oxidation with persulphate. Azo- group					8	Lanacyl violet, Victoria violet, &c.
			Decolourised. The colour returns on exposure to air :—Azine, Oxazine, or Thiazine group.					7	Red shade induline or fast blue R, &c.
			Decolourised. The colour does not return on exposure to air, but is restored upon oxidation with persulphate. Triphenylmethane group	The ammoniacal extract is colourless, but becomes violet on acidifying. Spot fibre with conc. HCl	No change			6	Red shade soluble blues.
					Becomes green			5	Alkali violets.
				The ammoniacal extract is violet or purple				4	Acid violets, formyl violets, &c.
			Not altered or only partially decolourised :—Pyrone group					3	Fast acid violets or violamines.
	Colour is nearly completely stripped :—Basic dyestuff. Boil with hydrosulphite A		Decolourised. The colour only returns on oxidation with persulphate :—Triphenylmethane group					2	Methyl violet, crystal violet, Hofmann violet, benzyl violet, &c.
			Decolourised. The colour returns on exposure to air :—Azine, Oxazine, or Thiazine group					1	Neutral violet, rhoduline violet, rosolane, iris violet, methylene violet, tannin heliotrope, &c.

[1] Alizarin on iron becomes brown on boiling with 5 p.c. acetic acid.

RECOGNITION OF DYES ON WOOL OR SILK.

TABLE IV.—BLUE COLOURS.

Boil twice for one minute with 5 p.c. acetic acid	Little or no colour is stripped:—Acid, Direct, or Mordant dyestuff. Boil twice for one minute with dilute ammonia (1 : 100) and small piece of white cotton. Keep the ammoniacal extract	Little or no colour is stripped. The cotton remains white (Mordant dyestuff) or is tinted (Direct dyestuff). Boil with 5 p.c. sodium acetate and white cotton for 2 or 3 minutes	The cotton remains white. Boil with a little aniline oil	The aniline solution is light-brown or colourless:—Mordant dyestuff. Confirm by testing ash for metallic mordants. Boil with hydrosulphite A	Decolourised. Colour is not restored either by air or persulphate:—Azo- group		20	A mordant azo-blue, *e.g.* cyprus blue, peri wool blue, anthracene chrome blue, chromotrope blue, &c.
					Decolourised. Colour does not return on exposure to air, but is restored by persulphate:—Triphenylmethane group		19	Chrome blue.
					Decolourised, but colour returns on exposure to air:—Oxazine or Thiazine group. Treat fibre with conc. H_2SO_4	Violet solution	18	Gallocyanins, celestin blue, gallamin blue, prune, &c.
						Green solution	17	Brilliant alizarin blue.
					Colour changed to dark-brown becoming blue again on exposure to air:—Alizarin group		16	An alizarin blue (anthraquinone-quinoline).
					Colour of wool unaltered:—Alizarin group		15	An alizarin cyanine, or anthracene blue.
				Blue solution which on evaporation to dryness leaves a residue which sublimes in violet vapours on heating			14	Indigo.
			The cotton is stained:—Direct dyestuff. On reduction with hydrosulphite A the colour is not restored either by air or persulphate:—Azo- group				13	Diamine, benzo, dianil, or Chicago blues, sulphone cyanines, &c.
		Much colour is stripped, but cotton remains white:—Acid dyestuff. Boil with hydrosulphite A	Not decolourised, but colour changed to bluish-red:—Alizarin group				12	Alizarin sapphirole, alizarin astrole, alizarin irisol, &c.
			Decolourised. Colour is not restored either by air or by persulphate:—Azo- group				11	An acid azo-blue, *e.g.* lanacyl blue, azo-acid blue, azo-merino blue, azo-navy blue, &c.
			Decolourised. Colour does not return on exposure to air, but is restored by persulphate:—Triphenylmethane group	Ammon. extract is colourless, but becomes blue on acidifying			10	A 'soluble' or 'alkali' blue (rosaniline blue).
				Ammon. extract is blue. On boiling with NaOH it becomes	violet		9	A dyestuff of the 'patent blue' class, *e.g.* patent blue V, A, N, &c. Cyanol, cyanine, ketone blue, erioglaucine, &c.
					colourless		8	A 'wool' blue.
			Decolourised and colour restored on exposure to air:—Azine, Oxazine, Thiazine, and Indigo group. Also Prussian blue	Ammon. extract is colourless. Fe in ash			7	Prussian blue.
				Ammon. extract is blue and on adding NaOH	becomes violet on heating		6	Thiocarmine, induline, fast blue.
					at once becomes yellow		5	Indigo extract, indigo carmine.
	Much colour is stripped. Boil with dilute alcohol (1 : 1) twice for one minute	Unaffected. Al or Cr or both are present in ash. The blue is changed to brick-red on spotting with HCl					4	Logwood blue.
		Much colour is stripped:—Basic dyestuff. Boil with hydrosulphite A	Decolourised. The colour does not return on exposure to air, but is restored by persulphate:—Triphenylmethane group				3	A basic blue of the triphenylmethane group, *e.g.* Victoria blue, night blue, brilliant milling blue B, &c.
			Decolourised. A violet colour returns on exposure to air:—Safranine azo-colour				2	A safranine-azo- colour, *e.g.* indoine or Janus blue.
			Decolourised. Original colour returns on exposure to air:—Azine, Oxazine, or Thiazine group				1	A basic blue of the azine, oxazine, or thiazine group, *e.g.* methylene blue, Nile blue, Capri blue, Meldola's blue, cresyl blue, &c.

RECOGNITION OF DYES ON WOOL OR SILK.

TABLE V.—GREEN COLOURS.

Boil twice for one minute with 5 p.c. acetic acid

The colour is stripped :—Basic dyestuff. Boil with hydrosulphite A			The colour is not stripped :—Acid, Direct, or Mordant dyestuff. Boil twice for one minute with dilute ammonia (1 : 100) and a small piece of white cotton								
			Much colour is stripped, but the cotton remains white :—Acid dyestuff. Boil with hydrosulphite A			Little or no colour is stripped. The cotton remains white (Mordant dyestuff) or is stained (Direct dyestuff). Boil for two or three minutes with 5 p.c. sodium acetate and a piece of white cotton					
							The cotton remains white [1] :—Mordant dyestuff. Confirm by testing for metallic mordant in ash. Boil with hydrosulphite A				
							Colour changes to brown :—Alizarin group		Decolourised (or changed to light buff)		
Decolourised. A dark-violet colour returns on exposure to air :—Safranine azo- colour	Decolourised. Original colour returns on exposure to air :—Azine, Oxazine, or Thiazine group	Decolourised. The colour does not return on exposure to air, but is restored by persulphate :—Triphenylmethane group	Decolourised. Colour returns on exposure to air :—Azine, Oxazine, or Thiazine group	Decolourised. Colour does not return on exposure to air, but is restored by persulphate :—Triphenylmethane group	Decolourised. Colour is not restored either by air or persulphate :—Azo- group	The cotton is deeply stained :—Direct dyestuff	Original colour returns on exposure to air	Original colour does not return on exposure to air, but is restored by persulphate	Colour returns on exposure to air :—Oxazine or Thiazine group	Colour does not return on exposure to air or upon oxidation with persulphate :—Nitroso- or Azo- group. Boil with conc. hydrochloric acid	
										Fibre and solution light-brown :—Nitroso- group	Fibre blue and solution colourless :—Azo- group
1	2	3	4	5	6	7	8	9	10	11	12
A safranine-azo- colour, *e.g.* Janus green or diazine green.	A basic green of the azine, thiazine, or oxazine group, *e.g.* fast green M, azine green, Capri green, methylene green, &c.	A basic green of the triphenylmethane group, *e.g.* malachite green, brilliant green, setoglaucine, fast green, &c.	Azine green S.	Acid greens, light green, guinea green, wool green, Neptune green, naphthalene green, &c.	Chiefly mixtures of an azo-blue and yellow.	Diamine green, Columbia green, chloramine green, benzo-green, &c.	Coerulein or alizarin green S.	Alizarin cyanine green or alizarin viridine.	Alizarin green G or B (oxazine group)	Nitroso-mordant colours, *e.g.* gambines, dioxine, dark green, naphthol green, &c.	Azo-mordant colour, *e.g.* diamond green, chrome patent green, &c.

[1] With azo- mordant colours the cotton may be slightly tinted, especially if the fixation by chrome is not complete.

RECOGNITION OF DYES ON WOOL OR SILK.

TABLE VI.—BROWN COLOURS.

Boil twice for one minute with 5 p.c. acetic acid							
Little or no colour is stripped:—Acid, Direct, or Mordant dyestuff. Boil twice for one minute with dilute ammonia							
Much colour is stripped:—Basic dyestuff. On boiling with hydrosulphite A decolourised, and colour does not return on exposure to air or on oxidation with persulphate:—Azo- group	Little or no colour is stripped:—Direct or Mordant dyestuff. Boil for two or three minutes with 5 p.c. sodium acetate and white cotton						
	Much colour is stripped:—Acid dyestuff. On boiling with hydrosulphite A decolourised, and colour does not return on exposure to air or on oxidation with persulphate:—Azo- group	The cotton is stained:—Direct dyestuff. Boil with hydrosulphite A	Decolourised, but colour not restored by air or persulphate:—Azo- group. Test ash for chromium to ascertain if chromed (cloth brown, chrome brown, &c.)			3	Diamine browns, benzo-browns, toluylene browns, Congo browns, Hessian browns, Columbia browns, dianil browns, sulphone browns, &c.
			Decolourised, but colour returns slowly on exposure to air or quickly on oxidation with persulphate:—Stilbene group			4	Mikado browns (stilbene group).
		The cotton remains white: Mordant dyestuff. Confirm by testing for metallic mordants in ash. Boil with hydrosulphite A	Colour not changed. Boil with dilute hydrochloric acid (1 : 10)	Colour is stripped		5	Anthragallol (anthracene brown).
				Colour not stripped		6	Cutch.
			Decolourised or changed to pale buff or light brown	Colour returns slowly on exposure to air or quickly on oxidation with persulphate		7	Chromogen.
				Colour not restored either by air or persulphate. Azo- group		8	Anthracene acid browns, acid anthracene brown, Palatine chrome brown, acid chrome brown, diamond brown, metachrome brown, &c. Also manganese brown (Mn in ash).
	Much colour is stripped:—Basic dyestuff. On boiling with hydrosulphite A decolourised, and colour does not return on exposure to air or on oxidation with persulphate:—Azo- group					1	Bismarck brown.
						2	Acid brown R, fast brown O, resorcin brown, naphthylamine brown, &c.

RECOGNITION OF DYES ON WOOL OR SILK.

TABLE VII.—BLACK AND GREY COLOURS.

Boil twice for one minute with 5 p.c. acetic acid

Much colour is stripped :— **Basic dyestuff** (N.B.—Logwood black on Fe mordant also becomes much paler though solution is not coloured)	**The colour is not stripped :—Acid, Direct, or Mordant dyestuff. Boil twice for one minute with dilute ammonia and a small piece of white cotton**									
	Much colour is stripped, but the cotton remains white :—Acid dyestuff. On boiling with hydrosulphite A the colour is permanently discharged	**The colour is not stripped :—Direct or Mordant dyestuff. Boil with 5 p.c. sodium acetate and small piece of white cotton**								
		The cotton is stained :—Direct or Azo-mordant dyestuff. Permanently decolourised by hydrosulphite A. Test ash for chromium		**The cotton remains white :—Mordant dyestuffs. (Confirm by testing ash for mordant.) Boil with dilute hydrochloric acid (1 : 10)**			**Not affected. Boil with hydrosulphite A**			
		Cr is absent: —Direct dyestuffs	Cr is present :—Mordant azo-dyestuffs	Fibre blue and solution crimson. Test for indigo by boiling with a little aniline : blue solution, which on evaporation to dryness gives residue subliming in violet vapour	Fibre and solution crimson	Fibre and solution pale brown	Becomes brown. Original colour slowly returns on exposure to air	Decolourised. Colour is not restored by exposure to air or by persulphate	Unaffected. Treat fibre with conc. H_2SO_4	
									Blue solution	Colourless solution
1	2	3	4	5	6	7	8	9	10	11
Diazine black, Janus black, methylene grey, &c.	Naphthol black, naphthylamine black, Palatine black, nerol, azo-merino black, &c.	Union black, half wool black, Columbia black, diamine blacks, dianil blacks, carbide blacks, &c.	Anthracene chrome blacks, Palatine chrome black, chromotropes, acid chrome black, chromate black, &c.	A 'vatted black' (indigo and logwood).	Logwood on Cr.	Logwood on Fe, or Bonsor's black.	Naphthazarine, alizarin blacks, alizarin blue black SW.	Diamond blacks.	Alizarin cyanine black.	Aniline black.

RECOGNITION OF DYES ON COTTON.

TABLE VIII.—YELLOW AND ORANGE COLOURS.

Boil with dilute ammonia (1 : 100)[1]

| The colour is stripped. Boil with acidified water and small piece of white wool | | |

RECOGNITION OF DYES ON COTTON.

TABLE IX.—RED COLOURS.

Boil with dilute ammonia (1 : 100)					
The colour is not stripped. Boil for half a minute with saline caustic soda, rinse, and boil twice for one minute with weak formic acid (1 : 100)					
The colour is not stripped or the acid extract is not precipitated by tannin solution. Reduce with hydrosulphite X					
Colour unaffected or changed to maroon or brown. Original colour restored on exposure to air :—Anthracene group. Boil with 90 p.c. formic acid. Also test ash for mordant	Colour but little affected by formic acid	Cr absent :—Anthracene vat dyestuff		16	Algole red B, indanthrene red, indanthrene claret.
		Cr in ash :—Anthracene mordant dyestuff		15	Alizarin purpurin or alizarin maroon on Cr mordant.
	Colour stripped by formic acid. Al in ash :—Anthracene mordant dyestuff			14	Turkey red, alizarin red, alizarin pink, alizarin maroon.
Colour changed to greenish yellow (not restored to original colour by air), which can be diazotised and developed red with *beta*-naphthol :—Primuline azo- colour				13	Primuline developed with β-naphthol or with R-salt.
Becomes yellow or colourless. Colour returns on exposure to air :—Azine or Indigo group. Apply lead acetate test. Also heat fibre in dry tube	No H_2S is evolved. Red vapours on heating :—Indigoid vat dyestuff			12	Algole red 5G and scarlet G, algole pink R, ciba red G and scarlet G, ciba bordeaux B, helindone red B and 3B, helindone scarlet S, helindone fast scarlet R, thioindigo red B, thioindigo scarlet, vat red.
	H_2S is evolved. No coloured vapours :—Sulphide dyestuff			11	Thiogene rubine, &c.
Decolourised and colour not restored by air or by persulphate :—Azo- group. Boil with soap solution and white mercerised cotton	The white cotton is not stained. Boil with pyridine	The colour is not stripped. Cr in ash :—Mordant azo- dyestuff		10	Chrome red, brilliant chrome red, chrome bordeaux, &c.
		The colour is stripped :—Insoluble azo- colour		9	Paranitraniline red, α-naphthylamine bordeaux, chloranisidine pink, nitroanisidine pink.
	The white cotton is stained :—Direct dyestuff. Test ash for Cr & Cu	Cr or Cu present :—Azo- direct dyestuff after-treated		8	Diamine fast red F, &c.
		No Cr or Cu present :—Azo- direct dyestuff		7	Benzopurpurine, diamine scarlets, diamine reds, benzo-fast scarlets, diazo-brilliant scarlet, rosanthrenes, Zambesi red, erica, diamine rose, geranine, rosophenine, &c.
The colour is completely or largely stripped, giving a coloured acid extract, which is precipitated by tannin solution :—Basic dyestuff (on tannin or other mordant). Transfer to wool and boil with hydrosulphite A		Wool decolourised. Colour not restored by air or by persulphate :—Azo- group		6	Janus red.
		Wool decolourised. Colour does not return on exposure to air, but is restored by persulphate :—Triphenylmethane group		5	Magenta, fuchsine, isorubine, cerise, grenadine, &c.
		Wool decolourised. Colour returns on exposure to air :—Azine group		4	Safranines, rhoduline reds and pink, azine scarlet, induline scarlet, neutral red, &c.
		Wool not decolourised :—Pyrone group		3	Rhodamines, rhodines, irisamine, acridine reds, &c.
The colour is stripped :—Acid dyestuff. Transfer to wool and boil with hydrosulphite B		Decolourised. Colour not restored by air or persulphate :—Azo- group		2	Crocein scarlets, brilliant croceines, fast reds, &c.
		Not decolourised :—Pyrone group		1	Eosins, phloxin, erythrosin, rose bengal, &c.

RECOGNITION OF DYES ON COTTON.

TABLE X.—PURPLE AND VIOLET COLOURS.

Boil with dilute ammonia (1 : 100)

The colour is stripped:—Acid dyestuff. The colour transferred to wool is decolourised by hydrosulphite A and restored by persulphate:—Triphenylmethane group

The colour is not stripped. Boil for half a minute with saline caustic soda, rinse, and boil twice for one minute with weak formic acid (1 : 100)

The colour is completely or largely stripped, giving a coloured acid extract, which is precipitated by tannin solution:—Basic dyestuff (on tannin or other mordant) or Basic mordant dyestuff. Boil with saline caustic soda, rinse well, and boil with small piece of white wool and plain water

The colour is not stripped or the acid extract is not precipitated by tannin solution. Reduce with hydrosulphite X

The colour is unaffected or only changed in shade, being restored to original on exposure to air:—Pyrone or Anthracene group. Test ash for mordant

		The wool is dyed:—Basic dyestuff. Boil wool with hydrosulphite A				The wool is not dyed. Cr is present in ash:—Basic mordant dyestuff. Boil cotton with hydrosulphite X		Decolourised and colour not restored by air or persulphate:—Azo- group or Alizarin on iron (decolourised slowly). Boil with soap solution and white mercerised cotton					Decolourised or yellowish. Colour restored on exposure to air:—Azine, Oxazine, Thiazine or Indigoid groups. Apply lead acetate test. Also heat fibre in dry test-tube			Al or Cr is present. Mordant dyestuff		Mordants are absent. Apply lead acetate test	
								The white cotton is stained: Direct dyestuff. Test ash for Cr and Cu		The white cotton is not stained. Boil with hydrochloric acid (1 : 20)				No H_2S is evolved. Test ash for mordant					
											The colour is not stripped. Boil with pyridine								
The ammoniacal solution is colourless, but becomes blue on acidifying	The ammoniacal solution is violet	Not decolourised:—Pyrone group	Decolourised. Colour returns on exposure to air:—Azine (Oxazine or Thiazine) group	Decolourised. Colour does not return in air, but is restored by persulphate:—Triphenylmethane group	Decolourised. Colour is not restored by air or persulphate:—Azo-group	Decolourised. Colour returns on exposure to air:—Oxazine group	Decolourised only slowly. Colour does not return in air, but is restored by persulphate:—Triphenylmethane group	No Cr or Cu present:—Azo-direct dyestuff	Cr or Cu present: Azo direct dyestuff after-treated	Colour destroyed, giving yellow solution. Fe present in ash:—Alizarin red on Fe mordant	The colour is stripped:—Insoluble azo-colour	The colour is not stripped. Cr present in ash: Mordant azo-dyestuff	H_2S is evolved. No coloured vapours on heating:—Sulphide dyestuff	Cr is present. No coloured vapours on heating:—Mordant oxazine dyestuff (not falling in group 7)	Cr is absent. Coloured vapours on heating:—Indigoid dyestuff	The colour on reduction is unchanged	The colour on reduction is browner or darker	H_2S is evolved:—Sulphide dyestuff	No H_2S is evolved:—Anthracene vat dyestuff
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
Red shades of soluble and alkali blues.	Acid violets, formyl violets, &c.	Anisoline.	Methylene violet, rhoduline violet, iris violet, neutral violet, tannin heliotrope, &c.	Methyl violets, ethyl violet, benzyl violet, crystal violet, &c.	Janus claret red, &c.[2]	Gallocyanine, gallamine blue, prune, &c.	Chrome violet.	Violets of the diamine, benzo, Congo, Hessian, Columbia, chlorazol, chlorantine, dianil, oxamine, and rosanthrene series.	Group 9 coppered or chromed.	Alizarin purple.[1]	Benzidine puce.	Chrome bordeaux, chrome prune, &c.	Thiogene violet, katigene violet, &c.	Gallamine blue, gallocyanine, &c.	Ciba violet, ciba heliotrope, thioindigo violet.	Gallein, alizarin violet, alizarin claret, alizarin cyclamine, alizarin on Cr mordant.	Alizarin cyanine 3R, alizarin bordeaux.	Thiogene dark red, &c.	Indanthrene violet or violanthrene.

[1] Alizarin on chromium becomes rather browner on reduction with hydrosulphite X.
[2] Janus claret red does not easily transfer to wool.

RECOGNITION OF DYES ON COTTON.

TABLE XI.—BLUE COLOURS.

Boil with dilute ammonia (1 : 100)

The colour is stripped:—Acid dyestuff (or Prussian blue)		The colour is not stripped. Boil for half a minute with saline caustic soda, rinse, and boil twice with weak formic acid (1 : 100)															
		The colour is completely or largely stripped, giving a coloured acid extract, which is precipitated by tannin solution:—Basic dyestuff (on tannin or other mordant) or Basic mordant dyestuff. Boil with saline caustic soda, rinse well, and boil with small piece of white wool and plain water					The colour is not stripped or the acid extract is not precipitated by tannin solution. Reduce with hydrosulphite X										
		The wool is dyed:—Basic dyestuff. Boil wool with hydrosulphite A			The wool is not dyed. Cr present in ash:—Basic mordant dyestuff. Boil cotton with hydrosulphite X		Decolourised and colour not restored by air or persulphate:—Azo- group. Boil with soap solution and white mercerised cotton			Decolourised or yellowish. Colour is restored on exposure to air:—Azine, Oxazine, Thiazine, or Indigo group. Apply lead acetate test			Colour changed to greenish-yellow, which can be diazotised and developed red with β-naphthol:—Primuline azo- colour	Colour unaffected or becomes darker, browner, &c., the original colour being restored on exposure to air:—Anthracene mordant or Anthracene vat dyestuff (also Ultramarine). Boil with 90 p.c. formic acid			
							The white cotton is stained:—Direct dyestuff. Test ash for Cr and Cu				No H_2S is evolved:—Heat fibre carefully in dry test-tube			The colour is stripped. Al in ash. Apply lead acetate test		The colour is not *much affected*. Test ash for Cr	
The extract is colourless, but becomes blue on acidification. Transferred to wool, the blue is decolourised by hydrosulphite A, and restored by persulphate:—Triphenylmethane group	The extract is colourless and remains so on acidification. $FeCl_3$ gives a blue precipitate	Decolourised. Colour returns on exposure to air:—Azine, Oxazine, or Thiazine group	Colour changes to red just before being decolourised. Colour returns violet or blue:—Safranine azo-dyestuff	Decolourised. Colour does not return on exposure to air, but is restored by persulphate:—Triphenylmethane group	Decolourised. Colour returns on exposure to air:—Oxazine group	Decolourised slowly. Colour restored only by persulphate:—Triphenylmethane group	No Cr or Cu present:—Azo-direct dyestuff	Cr or Cu present:—Azo-direct dyestuff after-treated	The white cotton is not stained. Colour is stripped by boiling pyridine:—Insoluble azo- colour	H_2S is evolved:—Sulphide dyestuff	Violet vapours evolved:—Indigoid dyestuff	No coloured vapour. Cr in ash:—Mordant thiazine or oxazine (not falling in Group 6)		H_2S is evolved	No H_2S evolved:—Alizarin dyestuff on Al	Cr present in ash:—Alizarin dyestuff on Cr	Cr absent:—Anthracene vat dyestuff
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Alkali[1] or soluble blues.	Prussian blue.	Methylene blue, new methylene blue, Nile blue, Capri blue, indazine blue, metaphenylene blue, Meldola's blue, fast blue, cresyl blue, rhoduline blue, nitroso-blue, &c.	Indoine blue, Janus blue, naphthindone blue, diazine blue, &c.	Victoria blue, night blue, turquoise blue, setocyanine, &c.	Gallocyanine, celestine blue, prune, &c.	Chrome blue.	Blues of the diamine, benzo, Congo, Columbia, chlorazol, dianil, oxamine, Chicago, &c., series.	Group 8 coppered or chromed.	Dianisidine blue.	Blues of the immedial, katigene, thiogene, pyrogene, sulphur, &c., series.	Indigo (natural and synthetic), indigo MLB, 2B, 4B, 5B, 6B, and T, ciba blue, bromindigo FB.	Brilliant alizarin blue, delphine blue, gallophenine, &c.	Primuline developed with naphthylamine ether.	Ultramarine.	Alizarin cyanines or anthracene blues on Al mordant.	Alizarin blue, alizarin cyanines or anthracene blues on Cr mordant.	Indanthrene blues, algol blues.

[1] Alkali blue dyed on a tannin and tin mordant is only partly stripped by weak ammonia, the solution being colourless.

RECOGNITION OF DYES ON COTTON.

TABLE XII.—GREEN COLOURS.

Boil with dilute ammonia (1 : 100)

The colour is not stripped. Boil for half a minute with saline caustic soda, rinse and boil twice with weak formic acid

The colour is not stripped nor the acid extract precipitated by tannin solution. Reduce with hydrosulphite X	The colour is completely or largely stripped, giving a coloured acid extract, which is precipitated by tannin solution :—Basic dyestuff (on tannin or other mordant) or Basic mordant dyestuff. Boil with saline caustic soda, rinse well, and boil with white wool and water	The wool is dyed :—Basic dyestuff. Boil wool with hydrosulphite A	Decolourised. Colour does not return on exposure to air, but is restored by persulphate :—Triphenylmethane group			4	Brilliant green, malachite green, methyl green, Victoria green, setoglaucine, &c.
			Colour becomes red just before being decolourised. Colour returns violet or green on exposure to air : —Safranine azo- group			3	Janus green, diazine green, &c.
			Decolourised. Colour returns on exposure to air :—Azine, Oxazine, or Thiazine group			2	Fast green M, methylene green, azine green, Capri green, &c.
		The wool is not dyed. Cr in ash. Cotton decolourised by hydrosulphite X, the colour not returning in air, but restored by persulphate :—Triphenylmethane group				5	Chrome green.
	Decolourised and colour not restored by air or persulphate :—Azo- or Nitroso- group. Boil with soap solution and white mercerised cotton	The white cotton is stained :—Direct dyestuff. Test ash for Cr and Cu	Cr and Cu absent : —Azo- direct dyestuff			6	Diamine green, benzo green, Columbia green, chloramine green, &c.
			Cr or Cu present : —Azo- direct dyestuff after-treated			7	Group 6 coppered or chromed.
		The white cotton is not stained. Boil with hydrochloric acid (1 : 20)	Colour destroyed. Fe is present in the ash :—Nitroso- group			8	Russian green, fast green, O, steam green, Alsace green, gambines, dioxine, &c.[1]
			Not decolourised. Cr is present in the ash :— Mordant azo- dye			9	Diamond green, &c.
	The colour is changed to greenish-yellow, not restored to green by air, but can be diazotised and developed red with β-naphthol :—Primuline azo- group					10	Primuline developed with aminodiphenylamine.
	Decolourised. Colour returns on exposure to air :—Azine, Oxazine, or Thiazine group. Apply lead acetate test	H_2S is evolved : —Sulphide dyestuff				11	Greens of the immedial, katigene, thiogene, pyrogene, sulphur, and thionol series.
		No H_2S is evolved : —Mordant oxazine (or thiazine) dye				12	Gallanilic green, indalizarin, &c.
	The colour is unaffected or changed to red, brown, blue, &c. Test ash for Cr and Ni	The ash contains Cr or Ni :—Anthracene mordant dyestuff	Reduced colour is brown. Green shade returns on exposure to air. Boil with hydrochloric acid (1 : 20)	Colour unaffected. Solution colourless. Cr in ash		14	Alizarin green S on Cr mordant.
				Colour of fibre becomes gray, solution red. Ni in ash		15	Alizarin green S on Ni or Mg mordant.
				Colour of fibre rather paler, solution brownish-yellow		16	Cœruleine, anthracene green.
			Reduced colour is brownish-red. Green restored by persulphate, but not by air. Boiling HCl (1 : 20) gives bright-green solution			13	Alizarin viridine, brilliant alizarin viridine.
		No Cr or Ni present in ash :—Anthracene vat dyestuff	Reduced colour is dark maroon. Green shade restored by air			18	Indanthrene green or viridanthrene, leucole dark green B.
			Reduced colour is blue. Green shade restored by air			19	Algole green, indanthrene blue in admixture with indanthrene yellow or with anthraflavone.
			Reduced colour is brownish-olive. H_2S evolved on applying lead acetate test			17	Indanthrene olive or olivanthrene.
	Reduced to yellow, which is restored by air oxidation :—Indigoid dyestuff					20	Ciba green.
	The colour is not stripped nor the acid extract precipitated by tannin solution. Reduce with hydrosulphite X	The colour is stripped :—Acid dyestuff. The colour transferred to wool is decolourised by hydrosulphite A and restored by persulphate :—Triphenylmethane group				1	Acid greens.

[1] Greens of the nitroso- group (gambines, &c.) may become black on reduction if the hydrosulphite X is insufficiently acid (formation of FeS).

RECOGNITION OF DYES ON COTTON.

TABLE XIII.—BROWN COLOURS.

Boil with dilute ammonia (1 : 100)

The colour is stripped :—Acid dyestuff. Transferred to wool, it is permanently decolourised by hydrosulphite A :—Azo- group	The colour is not stripped. Boil for half a minute with saline caustic soda, rinse, and boil twice with weak formic acid (1 : 100)											
	The colour is stripped, giving acid extract, which is precipitated by tannin solution :—Basic dyestuff. The dyestuff transferred to wool is permanently decolourised by hydrosulphite A :—Azo- group	The colour is not stripped or the acid extract is not precipitated by tannin solution. Reduce with hydrosulphite X										
		Decolourised and colour not restored on exposure to air or by persulphate :—Azo- group or mineral colours. Boil with soap solution and white mercerised cotton						The shade is changed to greenish-yellow, which can be diazotised and developed red with β-naphthol :—Primuline azo- colour	Decolourised and original colour restored by air :—Indigoid group	Unaltered or changed in shade, becoming darker, paler, yellower, &c. Apply lead acetate test		
		The white cotton is stained :—Direct dyestuff. Test ash for Cr and Cu		The white cotton is not stained. Boil with pyridine						No H_2S is evolved. Test ash for Cr and Cu		
				The colour is stripped :—Insoluble azo- colour. Test ash for Cu		The colour is not stripped :—Mineral colour. Treat with sodium bisulphite in the cold				Cr or Cu (or both) present :—Mordant dyestuff. Boil with HCl (1 : 20)		Cr and Cu absent :—Anthracene vat dyestuff, &c.
		Cr and Cu absent :—Azo- direct dyestuff	Cr or Cu present :—Azo- direct dyestuff after-treated	Cu absent	Cu present	Decolourised	Not decolourised			H_2S is evolved :—Sulphide dyestuff	Completely stripped	Not stripped or only slightly. Boil with dilute caustic soda 10 p.c.
												Fibre and solution dull violet	Solution brown, fibre unaffected	
		3	4	5	6	7	8	9	10	11	12	13	14	15
1	2	Browns of the diamine, benzo, Congo, dianil, Columbia, Hessian, oxamine, and toluylene series.	Group 3 coppered or chromed.	Para-brown (chrysoidine and paranitraniline), benzidine or toluidine brown.	Paranitraniline cutch (para-red coppered).	Manganese bronze.	Iron buff, khaki (oxides of Cr and Fe).[1]	Primuline developed with metaphenylene diamine. Terra-cotta, &c.	Helindone brown G.	Immedial cutch, cross dye brown, katigene browns, pyrogene browns, thiogene browns, &c.	Anthragallol, anthracene brown, alizarin brown.	Alizarin orange on Cr mordant, alizarin or purpurine on Cr.	Cutch.	Indanthrene maroon, algole brown, leucole browns, cibanone brown, paramine brown (*p*-phenylene diamine oxidised on fibre).
Fast brown, naphthylamine brown, acid brown, &c.	Bismarck brown, Janus brown, &c.													

[1] Iron buff and khaki may become black on reduction if the hydrosulphite X is insufficiently acid (formation of FeS).

RECOGNITION OF DYES ON COTTON.

TABLE XIV.—BLACK AND GREY COLOURS.

Boil with dilute ammonia (1:100)

The colour is not stripped. Boil with dilute hydrochloric acid (1:5)

The colour is not stripped (or only slightly). Boil for one minute with saline caustic soda, rinse, and boil with dilute hydrochloric acid (1:20)

The colour is not stripped nor acid extract precipitated by tannin solution. Reduce with hydrosulphite X

The colour is stripped					1	The colour is stripped:—**Acid dyestuff.** The dyestuff transferred to wool and boiled with hydrosulphite A is permanently decolourised:—Azo- group
					2	Solution red. Cr in ash
					3	Solution orange. Fe in ash
					4	Fibre and solution colourless
	The colour is largely stripped and the acid extract is precipitated by tannin solution:—Basic dyestuff. Transfer to wool and boil with hydrosulphite A				5	Decolourised. Colour returns on exposure to air:—Azine, Oxazine, or Thiazine group
					6	Colour becomes red just before being decolourised. Violet or violet blue colour returns in air:—Safranine azo-group
		The colour is not stripped nor acid extract precipitated by tannin solution. Reduces with hydrosulphite X	Decolourised and colour not restored by air or persulphate:—Azo- group. Boil with soap solution and white mercerised cotton	The white cotton is stained. Test ash for Cr and Cu	7	Cr and Cu absent:—Azo- direct dyestuff
					8	Cr or Cu present:—Azo- direct dyestuff after-treated
				The white cotton is not stained. Colour is stripped by boiling pyridine:—Insoluble azo-colour	9	Azophor black, &c.
			Decolourised and colour restored by air. Gives violet vapours on heating in dry tube:—Indigoid dyestuff		10	Ciba grey G and B.
			The reduced colour is brown, but is rapidly restored to black on exposure to air:—Azine, Oxazine, or Thiazine group. Apply lead acetate test	H_2S is evolved. Fibre becomes colourless or pale buff on boiling with bleaching powder solution 5°Tw.:—Sulphide dyestuff	11	Blacks of the immedial, katigene, cross dye, pyrogene, thiogene, thionol, pyrol, sulphur, &c., series.
				No H_2S is evolved. Fibre becomes reddish-brown on boiling with bleaching powder solution 5°Tw.:—An oxidation black	12	Aged aniline black, prussiate black, one bath aniline black, steam aniline black, diphenyl black.
			The colour is unaffected or changed in shade (becoming brown, maroon, &c.)	The reduced colour is brown. Only slowly and imperfectly restored to black by air but at once by persulphate. Cr present in ash:—Naphthalene mordant dyestuff	13	Naphthazarine S, alizarin black S, alizarin blue black SW, naphthomelane.
				Colour not changed by reduction (or very slightly):—Anthracene group. Test ash for Cr	14	Cr present:—Anthracene mordant dyestuff
					15	Cr absent:—Anthracene vat dyestuff

Indanthrene grey or melanthrene.

Alizarin cyanine black, alizarin blue black B.

Naphthazarine S, alizarin black S, alizarin blue black SW, naphthomelane.

Aged aniline black, prussiate black, one bath aniline black, steam aniline black, diphenyl black.

Blacks of the immedial, katigene, cross dye, pyrogene, thiogene, thionol, pyrol, sulphur, &c., series.

Ciba grey G and B.

Azophor black, &c.

Group 7 coppered or chromed.

Blacks of the diamine, oxydiamine, benzo, Columbia, dianil, Pluto, &c., series. Also diaminogen, diazo blacks, &c. (developed or coupled).

Janus black, Janus grey, diazine grey.

Methylene grey, new methylene grey, new fast grey, nigrisine, &c.

Logwood black on chrome mordant, noir reduit.

Logwood black on iron mordant.

Tannate of iron.

Naphthol blacks, naphthylamine blacks, Palatine black, &c.

DYER'S BROOM. *Genista tinctoria* (Linn.) (*Dyer's broom, Dyer's greenweed*; *Genet, Genestrole, Trentanel*, Fr.; *Ginster*, Ger.) is found in the pastures, thickets, and waste places throughout Central and Southern Europe, across Russian Asia to the Baikal, and northward to Southern Sweden. It is frequent in the greater part of England, but rare in Ireland and Scotland. The fact that it contains a yellow colouring matter is recorded by numerous writers, and the following embody the principal references to the dyeing and general properties of the plant: Bancroft (Philosophy of Permanent Colours, 1813, 2, 108); Gmelin (Handbook of Chemistry, 16, 517); Berthollet (On Dyeing, 1824, 2, 242); Gonfreville (Art de la Teinture de Laines, 501); Leuchs (Farben u. Farbekunde, 1846, 2, 309), and Schützenberger (Traite de Matières Colorantes, 1867, 4, 422).

To isolate the colouring matters, a hot aqueous extract of the plant is treated with lead acetate solution, and the pale-yellow viscous precipitate is collected and decomposed by means of boiling dilute sulphuric acid. The clear liquid decanted from the lead sulphate deposits on cooling a dull-yellow powder; this is filtered off, dissolved in a little alcohol, and the solution poured into a large volume of ether, causing the separation of a dark-coloured resinous impurity. The clear liquid is evaporated, yielding a yellow crystalline residue, which consists of two substances. To separate these advantage is taken of the fact that, with sulphuric acid in the presence of acetic acid, one only of these compounds gives an insoluble sulphate. This is collected and decomposed with water and the product crystallised from dilute alcohol. It is obtained as yellow needles, and was found to be identical with the *luteolin* of weld. (*Reseda luteola*) (Perkin and Newbury, Chem. Soc. Trans. 1899, 75, 830).

Genistein $C_{14}H_{10}O_5$, the second colouring matter of dyer's broom, is present in the mother liquors obtained during the purification of the luteolin, and also in considerable quantity in the filtrate from the lead precipitate, from which it is most readily isolated. To the boiling liquid ammonia is added, causing the separation of a lemon-yellow precipitate, which is collected and decomposed with boiling dilute sulphuric acid. The clear liquid is extracted with ether, and the extract evaporated, leaving a brownish crystalline mass. It is purified by crystallisation from acetic acid, and by conversion into the acetyl derivative.

Genistein crystallises in long colourless needles; m.p. 291°–293° (Perkin and Horsfall, Chem. Soc. Trans. 1900, 77, 1312); soluble in alkalis with a pale-yellow colouration. Alcoholic ferric chloride gives a dull-red violet colouration, and alcoholic basic lead acetate a lemon-yellow precipitate.

Triacetylgenistein $C_{14}H_7O_5(C_2H_3O)_3$, colourless needles, m.p. 197°–201°; and *tetrabromgenistein* $C_{14}H_6Br_4O_5$, colourless needles, m.p. above 290°, have been described.

On digestion with boiling 50 p.c. potassium hydroxide, genistein gives *phloroglucinol* and *p-hydroxyphenylacetic acid.*

By methylation with methyl iodide in the usual manner, genistein dimethyl ether and methylgenistein dimethyl ether are produced.

Genistein dimethyl ether $C_{14}H_8O_3(OCH_3)_2$, forms colourless leaflets, melts at 137°–139°, and gives the *monacetyl* compound,

$$C_{14}H_7O_3(C_2H_3O)(OCH_3)_2,$$

in minute colourless needles, m.p. 202°–204°. When decomposed with alcoholic potash, it forms *methoxyphenylacetic acid* and *phloroglucinol-monomethyl ether* (identified by means of its disazobenzene derivative).

Methylgenistein dimethyl ether

$$CH_3{\cdot}C_{14}H_7O_3(OCH_3)_2,$$

melts at 202°; and the *acetyl* derivative

$$CH_3{\cdot}C_{14}H_6O_3(C_2H_3O)(OCH_3)_2$$

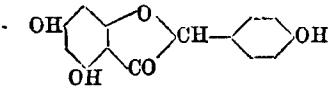
forms colourless needles, m.p. 212–214°. With alcoholic potash, *methoxyphenylacetic acid* and probably *methylphloroglucinolmonomethyl ether* are obtained.

Genistein diethyl ether $C_{14}H_8O_3(OC_2H_5)_2$, forms colourless needles, m.p. 132°–134°; whereas *acetylgenistein diethyl ether*

$$C_{14}H_7O_3(C_2H_3O)(OC_2H_5)_2$$

melts at 168°–170°. Alcoholic potash gives *p-ethoxyphenylacetic acid.*

According to Perkin and Horsfall, genistein is most probably a *trihydroxyphenylketocumaran*



Genistein is a feeble colouring matter, and upon woollen cloth gives, with chromium mordant, a pale greenish-yellow; with aluminium mordant, a very pale-yellow; and with iron mordant, a chocolate-brown shade.

Dyeing properties of dyer's broom.—In this respect there is a close resemblance between dyer's broom and weld. The dyeing power of the former is distinctly the weaker of the two; otherwise the only point of difference worthy of mention is that shown by the iron mordant, which, in the case of dyer's broom, gives a duller and more drab-coloured shade. A. G. P.

DYNAMAGNITE, DYNAMITE *v.* EXPLOSIVES.

DYSCRASITE. Silver antimonide (*v.* ANTIMONY).

DYSODILE. A soft laminated carbonaceous substance of a yellowish-grey or green colour, burning with a luminous flame, and a smell resembling that of burning caoutchouc. Found in Sicily and in Bavaria (Fricklinger, Jahrb. Min. 1875, 760; also Church, Chem. News, 34, 155; Potonié, Chem. Zentr. 1907, ii. 555).

DYSPROSIUM. Sym. Dy. At. wt. 162·5. (Urbain and Domenitroux, Compt. rend. 1906, 143, 598; Hinrichs, *ibid.* 1143.) From erbia—one of the fractions obtained from ytterbite—Cleve separated an earth which he called 'holmia'; and from this material Lecoq de Boisbaudran isolated a simpler constituent, *dysprosia*, characterised by a well-marked absorption spectrum showing bands in the ultra-violet as well as in the visible region of the spectrum (Compt. rend. 1886, 102, 100). This oxide, one of the most basic constituents of holmia, was concentrated by precipitations with potassium sulphate and ammonia. Further fractionation of the nitrates and double nitrates gave a product rich in terbium and dysprosium (Urbain, Compt.

rend. 1904, 139, 736; 1905, 141, 521). The latter is separated from terbium by fractional crystallisation of the ethyl sulphates, terbium and yttrium being concentrated in the least soluble fraction, whilst dysprosium accumulates in the middle fraction (Urbain, Ann. Chim. Phys. 1900, [7] 19, 184; Compt. rend. 1906, 142, 785).

Dysprosium is separated from yttrium by crystallisation of the nitrate with the addition of bismuth nitrate.

Dysprosium forms a white *oxide* Dy_2O_3, but no peroxide. Its salts have a faint greenish-yellow tint: *chloride* $DyCl_3,6H_2O$; *nitrate* $Dy(NO_3)_3,5H_2O$, melting at 88° in its water of crystallisation, very similar to bismuth nitrate (Urbain and Jantsch, Compt. rend. 1908, 146, 127); *sulphate* $Dy_2(SO_4)_3,8H_2O$, brilliant yellowish crystals, stable at 110°, and completely dehydrated at 360°. For other salts, *v.* Jantsch and Ohl, Ber. 1911, 44, 1274.

Dysprosium stands first in the list of paramagnetic elements, its oxide Dy_2O_3 being 12·8 times more magnetic than ferric oxide. The high values for the magnetic susceptibility of the rare earths (yttria, erbia, &c.) fractionated by Cleve and Nilson are probably due to the presence of dysprosium (Urbain, Compt. rend. 1908, 146, 922).

G. T. M.

E

EARTHNUT OIL *v.* ARACHIS OIL.

EAU DE COLOGNE *v.* PERFUMES.

EAU DE JAVELLE. Solution of sodium hypochlorite (*v. Bleach liquor*, art. CHLORINE).

EAU DE LUCE. *Aqua luciæ.* A milky liquid containing oil of amber, alcohol, and ammonia (*v.* AMBER, OIL OF).

EBONITE. *Sulphurised caoutchouc* (*v.* RUBBER).

EBULLIOSCOPE. An instrument for determining the strength of spirits of wine by means of its boiling-point.

ECBOLINE *v.* ERGOT OF RYE.

ECGONINE *v.* VEGETO-ALKALOIDS.

ECHITAMINE, ECHITENINE *v.* DITA BARK.

E. C. POWDER *v.* EXPLOSIVES.

EDESTIN. A crystalline proteid substance found in the seeds of hemp, sunflower, and castor-bean, capable of uniting with acids to form salts (Osborne, J. Amer. Chem. Soc. 24, 39).

EDIBLE OILS AND FATS. Under this term are comprised those oils and fats which serve as food. Most of the edible oils and fats, such as olive oil, cod liver oil, suet, lard, butter-fat, cacao butter, goose fat, &c., are immediately fit for consumption, if 'rendered' with sufficient care. Hence they rarely need undergo a process of technical purification, except simple filtration, before they are placed on the market. This applies, however, only to the freshly ('first') rendered products, as contact with putrescible organic matter rapidly causes hydrolysis of the oils and fats, so that, *e.g.*, lard or olive oil which has been allowed to remain in contact for some little time with the organic tissues from which they have been derived, readily become rancid, and therefore unfit for food in their original state. This applies with especial force to cod liver oil.

The large demand made on the market by the rapidly growing consumption of oils and fats has, however, led to the employment of second and even third 'renderings,' in the case of animal fats, and second or third 'expressions' in the case of vegetable oils and fats. Such products contain, as a rule, notable amounts of free fatty acids, and small quantities of extractive substances, all of which must be removed before the oils and fats become suitable for food purposes. The processes applied to the purification and decolourisation are treated as deep secrets. It may, however, be stated that most of the processes are based on physical methods of refining (*see* OILS AND FATS).

Chemicals involving the use of mineral acids must be altogether excluded from the purview of the refiner, since the mineral acids, however carefully they may be removed by subsequent washing, impart an objectionable flavour to the products, thus rendering them useless for edible purposes. Alkalis or alkaline earths are not so objectionable, and are, therefore, used commercially for the removal of free fatty acids. (A notable example of this kind is furnished by the usual method of refining cotton-seed oil.) The alkalis and alkaline salts chiefly employed in practice are caustic soda, sodium carbonate, lime, and magnesia. Baryta has also been proposed (and patented), but its poisonous properties would prohibit its use.

Whereas all animal oils and fats, when freshly prepared, are suitable for food, this holds good only in a somewhat restricted sense of vegetable oils and fats. If the vegetable oils and fats are free from objectionable substances they may hold in solution or may have dissolved from the vegetable matter from which they have been obtained by expression or boiling out, then they are suitable for edible purposes, and are so used to a very considerable extent.

We know, however, a number of oils which contain non-fatty toxic or injurious substances, such as tung oil, calophyllum oil, curcas oil, croton oil. In the case of castor oil, the fatty acids themselves are injurious to health; hence castor oil is unusable as a foodstuff. Experience has also shown that the fats belonging to the Chaulmoogra group are injurious to health. All these oils must, therefore, be excluded from the list of edible oils.

With regard to the palatableness of the edible oils and fats, much depends on the demand made in that respect by the population of the various countries of the world. Thus, whereas rape oil and linseed oil find a ready market for edible purposes in India, these oils are at present

used in exceptional cases only as table oils in Western Europe. They are replaced in richer countries by cotton-seed oil, sesamé oil, arachis oil, poppy-seed oil, and olive oil. The increased consumption of the available edible oils and fats has created, during the last decade, a new and growing industry.

Amongst the most important developments in this industry is the preparation of cocoa-nut oil and palm-kernel oils for edible purposes (*see* COCOA-NUT OIL and PALM-KERNEL OIL). Mixtures of several edible oils are now largely prepared as 'table oils' to replace olive oil. Amongst these substitutes the most important are: arachis oil, sesamé oil, cotton-seed oil, and to some extent also soya-bean oil. Mixtures of edible vegetable and animal oils and fats are chiefly represented by the 'suet substitutes,' which are prepared by mixing tallow with cotton-seed oil, and by 'lard substitutes,' which represent a mixture of animal fats with cotton-seed oil, maize oil, &c. Up to recently, 'compound lard' contained frequently no lard whatever, but, according to recent legislation in the United States, 'lard compounds' or 'lard substitutes' must contain at least 50 p.c. of lard (*see* LARD SUBSTITUTES).

The manufacture and sale of edible oils and fats has assumed such considerable importance that legislation has stepped in to protect the public against fraudulent practices both as regards the commercial description of a 'blended' fat and the absence of injurious substances (*see* MARGARINE). J. L.

EDULCORATION. The act of washing insoluble matter so as to remove any soluble impurity.

EFFLORESCENCE. This term is applied to two or three different phenomena, characterised by the formation of a loose pulverulent deposit on the surface of a solid body.

1. Crystallised salts are said to effloresce when they lose their water of crystallisation and fall to powder, *e.g.* normal sodium carbonate.

2. The formation of a pulverulent crystalline deposit on the surface of a porous body, in consequence of the crystallisation of a salt existing in solution within its pores, or formed from materials existing therein, is also called efflorescence; *e.g.* the crystallisation of potassium nitrate on the surface of the earth or in caves, as in India, or on saltpetre plantations; of sodium sulphate and carbonate on walls; of alum on alum-slate; of ferrous sulphate on iron pyrites, &c. In all these cases the solution of the salt is drawn by capillary action to the surface of the solid body, and there crystallises in consequence of the evaporation of the water.

3. The term 'efflorescence' is likewise applied to the effect which sometimes takes place when a saline solution is left to evaporate slowly in an open vessel. The solid salt separates in dendritic crystals just where the surface of the liquid touches the side of the vessel, and the solution, rising by capillarity between these crystals, forms a fresh crystallisation just above the first layer; and this process is continually repeated till the crystallisation thus formed extends over the edge of the vessel, and sometimes down to the table on which it stands. Sal-ammoniac and other ammonia salts often effloresce in this manner. The effect may be prevented to a certain extent by greasing the edge of the vessel, or better, by quickly boiling the solution, or evaporating it by heat from above.

EGG. The egg of the common fowl, *Gallus Bankiva*, consists of four principal parts: the *shell*; the *white*; the *yolk* or *vitellum*; the *white yolk* or *germinal cell*; and the membranes separating these parts. The usual weight of an egg is 40–60 grams; of this the shell and shell membrane form 5–8 grams; the yolk, 12–18 grams; and the white, 23–34 grams.

The shell has the composition:

Calcium carbonate . . .	89·6 p.c.
Phosphates of lime and magnesia	5·7 „
Organic matter and sulphur .	4·7 „

The colouring matter of egg-shells is a bile pigment (Liebermann, Ber. 11, 606).

The *shell membrane* or *membrana putaminis* separating the white from the shell is double, the two parts being in contact over the greater part of the inner surface of the shell, but separated by an air-space at the broad end of the egg. These membranes are composed of a proteid substance allied to keratin (Liebermann).

Abderhalden and Strauss have examined the products of hydrolysis of *ovokeratin*, and find them to be, from 100 grams of substance: 3·9 grams glycine; 3·5 grams alanine; 1·1 gram amino-valeric acid; 7·4 grams leucine; 4·0 grams proline; 8·1 grams glutamic acid; and 1·1 gram aspartic acid (Zeitsch. physiol. Chem. 1906, 48, 530).

The white is a faintly yellow albuminous fluid enclosed in large cells of thin membrane. The fluid has sp.gr. 1·045, and is really mobile, though it appears viscous because of its confinement by the cell walls. It has an alkaline reaction. The constituents are:

Water	85–88 p.c.
Proteid bodies . . .	10–13 „
Salts	0·7 „
Fermentable sugars . .	0·5 „

with traces of fats, soaps, lecithin, and cholesterol. Salkowski states that the fermentable sugar is glucose (Chem. Soc. Abstr. 1894, i. 214).

The protein substances of egg white are all gluco-proteids, and in their solution and precipitation properties are similar to globulins, albumins, or proteoses (*v.* art. PROTEINS).

Ovoglobulin separates from egg white partly on dilution with water, and completely if the solution be saturated with magnesium sulphate or ammonium sulphate. By repeated solution in water and reprecipitation, part becomes insoluble (Langstein, Hofmeister's Beitrage, 1), and it is probably a mixture of several globulins (Corin and Berard, Bull. Acad. Belg. [3], 15, 643). The globulins form about 6·7 p.c. of the total proteids of egg white (Dillner, Hammarstein's Text-book Physiol. Chem. 430).

Ovalbumin is the chief proteid constituent of egg-white. It is obtained crystalline by precipitating the globulins with ammonium sulphate, as above, and allowing the filtrate to evaporate. (For details of methods, *see* Hofmeister, Zeitsch. physiol. Chem. 16, 187; Osborne and Campbell, J. Amer. Chem. Soc. 1900, 22, 422; Rosenkrantz, J. Russ. Phys. Chem. Soc. 1906, 38, 2; and Mayer, Compt. rend. 1906, 143, 515.)

Pure ovalbumin crystallises in large, well-formed needles. A 2·5 p.c. solution in water

becomes turbid at 60°, and at 64° yields a flocculent coagulum. The addition of sodium chloride to the solution raises the temperature of coagulation (Osborne and Campbell, *l.c.*; Stärke, Pflüger's Archiv. 12, 18).

The composition of ovalbumin is:

C	H	N	S	P	O
52·75	7·10	15·51	1·62	0·12	22·90 p.c.

(Osborne and Campbell, *l.c.* 441; in agreement with Hopkins, J. Physiol. 25, 306; and Hammarsten, Zeitsch. physiol. Chem. 9, 304).

Many attempts have been made to assign a formula to ovalbumin. Latham (Biochem. J. 1908, 3, 207 *et seq*) gives it a molecular weight of 5473, and the formula $C_{240}H_{397}N_{65}O_{75}S_3$, but this must be regarded as an approximation only.

It has been characterised by determining the various amino-acids yielded on hydrolysis with hydrochloric acid of sp.gr. 1·19 (*v.* art. PROTEINS). 100 grams ovalbumin yield: alanine, 2·1 grams; leucine, 20·0 grams; phenylalanine, 4·4 grams; tyrosine, 1·1 gram; cystine, 0·3 gram; proline, 2·3 grams; aspartic acid, 1·5 grams; and glutamic acid, 8·0 grams (Abderhalden and Pregl, Zeitsch. physiol. Chem. 1905, 46, 24; Osborne, Jones, and Leavenworth, Amer. J. Physiol. 1909, 24, 252; Levene and Beatty, Biochem. Zeitsch. 1907, 4, 305).

The specific rotation of pure albumin is given as −31° (Willcock, J. Physiol. 1908, 37, 27), −30·70° (Hopkins, *ibid.* 25, 306), and −29·31° (Osborne and Campbell, *l.c.*).

The precipitation of albumin by acids and salts is a completely reversible reaction (Galeotti, Zeitsch. physiol. Chem. 1905, 44, 461), and follows the law of mass action (Ostwald, Chem. Soc. Abstr. 1908, i. 375; Gerrini, Zeitsch. physiol. Chem. 1906, 47, 287).

Conalbumin. Only about one-half of the proteid of egg white can be obtained as crystallised ovalbumin; the other fractions have a higher rotation and sulphur content. By heating these fractions at 65°, *conalbumin* is obtained as a coagulum, which, when dried at 110°, has the following composition:—

C	H	N	S	O
52·25	6·99	16·11	1·70	22·95 p.c.

Its specific rotation is about −36° (Osborne and Campbell, *l.c.*; Panormoff, Chem. Zentr. 1898, 11, 487).

Ovomucoid is found in the residue after all proteids coagulated by heat have been removed from egg white (Neumeister, Zeitsch. Biol. 1890, 27, 369; Mörner, Zeitsch. physiol. Chem. 1893, 18, 525). It forms about 10 p.c. of the proteids of egg white. It is not precipitated from solution by mineral acids or organic acids (except phosphotungstic and tannic acids) or by metallic salts.

The *inorganic constituents* of egg-white in 1000 parts are: Potash, 276–285 parts; soda, 235–329 parts; lime, 18–29 parts; magnesia, 16–32 parts; iron oxide, 4·4–5·5 parts; chlorine, 238–205 parts; phosphoric acid, 32–48 parts; sulphuric acid, 13–26 parts; silica, 3–20 parts; carbon dioxide, 97–116 parts (Poleck and Weber, Hammarsten's Physiol. Chem. 1904, 432). Traces of fluorine have also been found (Nickles, Compt. rend. 43, 885).

The **yolk** or yellow is contained within a membrane composed of a proteid allied to keratin (Liebermann, Pflüger's Archiv. 43). It is a viscous, opaque, yellow, alkaline emulsion having a mild taste, and consists chiefly of water, fats, and colouring matter, together with vitellin, lecithin, cholesterol, &c. Müller and Masuyama (Zeitsch. f. Biol. 1900, 39, 542) have found a diastatic enzyme in the yolk; and the presence of purine bases has been detected by Mesernitzki (Biochem. Zentr. 1, 739).

1000 parts of the yolk contain approximately: water, 480 parts; fats, 228·4 parts; proteid (vitellin), 156·3 parts; lecithin, 107·2 parts; cholesterol, 17·5 parts; insoluble salts, 6·12 parts; soluble salts, 3·53 parts.

According to Poleck, the ash of yolk of eggs contains, in 1000 parts: soda, 51·2–65·7 parts; potash, 80·5–89·3 parts; lime, 122·1–132·1 parts; magnesia, 20·7–21·1 parts; iron oxide, 11·9–14·5 parts; phosphoric acid, 638·1–667·0 parts; silicic acid, 5·5–14·0 parts.

The *fat* forms about 30 p.c. of the yolk, and may be extracted with ether. It is a mixture of solid and liquid fat, and contains 0·6 p.c. phosphorus, equivalent to 15·04 p.c. lecithin; 61·5 p.c. of neutral fat; and 23·2 p.c. free acids. The neutral fat contains glycerol and acid in such proportions as prove it to consist of *triglycerides* only (Thorpe, Arch. Nedér. Sci. Exact. Nat. 1901, 6, 155). On saponification it yields 40 p.c. oleic acid; 38·04 p.c. palmitic acid; and 15·21 p.c. stearic acid (Paladino, Biochem. Zeitsch. 1909, 17, 356).

Barbieri, by extracting yolks with carbon disulphide, obtained tristearin and triolein (Compt. rend. 1907, 145, 133), besides cholesterol; while MacLean has isolated pure tripalmitin from egg-fat (Biochem. J. 1909, 4, 168).

Berthelot and André have determined the heat of combustion of egg yolk to be 8124 calories per gram, as compared with about 5000 calories per gram for most other constituents of foodstuffs (Compt. rend. 110, 925).

Lutein, the colouring matter, is a mixture of two substances: *vitellolutein*, which is yellow, and soluble in petroleum; and *vitellorubrin*, a red body, soluble in carbon disulphide (Maly, Chem. Zentr. 1881, 485). The mixture is an orange-red amorphous substance, which is not affected by alkalis, and can, therefore, be isolated by hydrolysing the fats. It has been suggested that the characteristic spectroscopic behaviour of the lutein should be used to judge the purity of commercial dried egg yolk (Lewin, Miethe, and Stenger, Pflüger's Archiv. 1908, 124, 585).

Lecithin is present both free and in combination with proteid (Manasse, Biochem. Zeitsch. 1906, 1, 246), and may be obtained by extracting yolks repeatedly with alcohol, distilling off the alcohol from the united extracts under reduced pressure, adding ether to the syrupy product, and finally precipitating with acetone (Roaf and Edie, Chem. Soc. Abstr. 1905, ii. 364).

Phosphorus is present in the yolk, chiefly as lecithin and lecithin phosphoric acid, and it has been suggested that egg yolk could be estimated by igniting with a little sodium carbonate and nitre, and estimating the phosphoric acid in the residue. 1·129 gram of phosphoric acid represents 100 grams of yolks (Bein, Ber. 23, 423). The addition of alkali is necessary to prevent

loss of phosphoric acid during ignition (Juckenack, Zeitsch. Nahr. Genussm. 1899, 905).

Cholesterol occurs in the yolk to the extent of about 1 p.c. (Juckenack, *l.c.*; Benecke, Bied. Zentr. 1881, 568).

Vitellin, the proteid constituent of the yolk, is separated by mixing the yolks with brine, in which the proteid is soluble, and extracting the fat, &c., with ether. It has the properties of a globulin, and, on dialysis or dilution of the solution, is precipitated as a white granular substance. A solution coagulates at 70°–75°.

Vitellin thus obtained is a mixture of compounds of protein matter with lecithin, containing from 15–30 p.c. of the latter, called *lecithin-nucleovitellins*. The lecithin thus combined is not removed by ether, but is completely removed by alcohol, leaving an insoluble proteid, *nucleovitellin*, of constant composition, which, on digesting with pepsin, yields paranuclein.

It is probable that all these proteids are compounds of vitellin with phosphoric acid H_3PO_4, or some very simple organo-phosphoric acid. The composition of vitellin, free from phosphoric acid, is:

C	H	N	S	O
52·71	7·46	16·64	1·05	22·14 p.c.

(Osborne and Campbell, J. Amer. Chem. Soc. 1900, 22, 413).

Plimmer states that another distinct proteid '*livetin*,' can be obtained from the yolk (Chem. Soc. Trans. 1908, 1500).

The germinal vesicle, or white yolk, forms a layer between the yolk and the yolk membrane, with a process extending to the centre of the yolk. It is enclosed in a membrane, and contains proteids, lecithin, and a nuclein rich in phosphorus (Meischer, Chem. Soc. Trans. 1871, 24, 746).

The space between the shell membranes at the broad end of the egg contains a mixture of oxygen, nitrogen, and carbon dioxide, richer in oxygen than the surrounding air (Hufner, Du Bois Reymond's Archiv. de Physiol. 1892, Phys. Abth. 54.

Eggs contain, on the average, about 4·6 mgms. of ferric oxide. This amount is increased by feeding the hens with foods rich in iron, and '*iron-eggs*' thus obtained have been recommended for therapeutic use, but are very costly (Hartung, Zeitsch. f. Biol. 1902, 43, 195; Hofmann, Zeitsch. anal. Chem. 1901, 40, 450).

Bertrand states that arsenic is normally present in the egg to the extent of $\frac{1}{200}$ mgm. (Compt. rend. 1903, 136, 1083).

Development.—During incubation, the egg respires, giving off carbon dioxide and water, and absorbing oxygen. If this process be stopped by placing the egg in an inert gas, or by rendering the shell impervious to gases, the development of the chick ceases. The respiration is slight for the first four days of incubation, and then increases until, at the ninth day, the respiration of the egg is equal to that of a fowl, weight for weight. This respiration involves combustion of the fat of the egg, and a steady loss in weight (Pott, Landw. Versuchs. Stat. 23, 203; Chem. Soc. Abstr. 1879, 474).

Levene states that the quantity of xanthine bases and nuclein compounds increases with the growth of the embryo (Amer. J. Physiol. 1900, 3, xii.).

All the phosphorus in the chick is derived from the yolk and white, and, until the last few days of incubation, no lime is taken from the shell (Voit, Zeitsch. f. Biol. 13, 518; Pott, *l.c.*). At the end of incubation, the shell may supply some of the lime required (Carpiaux, Bull. Acad. Roy. Belg. 1903, 283; *see* also Plimmer and Scott, J. Physiol. 1909, 38, 247).

The freezing-point of fresh eggs is 0·427°–0·480°, and rises slightly as incubation proceeds, corresponding to a rise of osmotic pressure from 5·5 atmospheres to 7·3 atmospheres (Atkins, Biochem. J. 1909, 480).

The chief *uses of eggs* are as an article of food and in the tanning industry. As the supply of new-laid eggs varies with the season, recourse is had to some means of preserving a proportion of those that come into the market at the time of greatest production.

The following is a list of some processes for preserving whole eggs, which have been patented.

Saturating with carbon dioxide (Lake, Eng. Pat. 1653, 1888); wrapping air-tight in rubber-coated paper (Jessen, Eng. Pat. 15580, 1891); coating with gelatin (Mills, Eng. Pat. 17717, 1891; Farquhar and North, Eng. Pat. 15128, 1892; Coakley, Eng. Pat. 18816, 1899); with gelatinous starch solution (Schultz, Eng. Pat. 1328, 1902); with drying oils, wax, or varnish, with or without previous treatment with antiseptics (Stukes, U.S. Pat. 649899; Barlow, Eng. Pat. 11054, 1902; Lorne, Eng. Pat. 18439, 1901, and 9898, 1901); with boric acid (Markham, Eng. Pat. 3513, 1895); with lime (McArdle, Eng. Pat. 3592, 1892; Wilson and Wilson, Eng. Pat. 15461, 1899); with sulphuric acid (Reinhardt, Eng. Pat. 18130, 1898; Marks, Eng. Pat. 12867, 1903); and with water-glass (Stead, Eng. Pat. 4910, 1882; Rylander, Eng. Pat. 23523, 1901).

Comparative tests have been made (J. Soc. Arts, 1898, 46, 370; J. Soc. Chem. Ind. 1898, 261), which show that the only methods which keep over 90 p.c. of the eggs in good condition for 8 months are: (1) varnishing with vaseline; (2) keeping in milk of lime; and (3) keeping in water-glass solution. Of these the last method is the one least open to objection, and is that chiefly used. Eggs preserved in water-glass have a tendency to burst when boiled, but this can be prevented by piercing the shell with a needle.

The contents of eggs may be preserved by heating at 185°F. with a strong solution of a sugar (glucose, maltose, dextrose, &c.), until the product contains 40–60 p.c. of sugar. It is readily miscible with water, milk, &c., and will keep for some months without deterioration (Fordred, Eng. Pat. 15762, 1894; Goodlett, U.S. Pat. 692268).

An important method of preserving the whites and yolks of eggs consists in drying the mixture in a current of air at 37°–40° during 18 hours, powdering the product, and again exposing to dry air. The powder is packed in tins, or can be pressed into tablets, and is quite soluble in water (Foschi, Fr. Pat. 369967, 1906). A similar product is obtained by drying on a hot roller at a temperature above 212°F. (Hatmaker, Eng. Pat. 28, 1905; *see also* Eng. Pat. 8743, 1903, for apparatus).

Substitutes for eggs in baking are made from albumin and casein obtained from skimmed

milk, sometimes mixed with a proportion of dried egg; or from maize meal containing sodium bicarbonate and artificial colouring matter (Beythien and Waters, Zeitsch. Nahr. Genussm. 1906, 11, 272; Bernstein, Eng. Pat. 14336 and 29189 of 1897).

The eggs used for the treatment of leather, especially the finer sorts of glove leather, are preserved in the liquid state by the addition of salt and borax (Jean, Mon. Sci. 1892, 6, 561). Analyses of this material, '*eggio*,' show that it contains 2–5 p.c. more water and 3½–6 p.c. less fatty acid than fresh egg yolk (Boyer, J. Soc. Chem. Ind. 1892, 447). Bein has pointed out that the addition of salt to yolks materially reduces the amount of fat (Bied. Zentr. 21, 138). Rotten eggs could well be used for this purpose, as Cech has found that the available oil is not much diminished in amount, and can be extracted by pressure (J. pr. Chem. [2] 22, 338).

Oil of egg, obtained by extracting yolks with ether, forms about 10 p.c. of the egg, and is used in pharmacy in the preparation of ointments and emulsions. It has no medicinal value (Paladino and Toso, Analyst, 1896, 21, 161). It has the following properties: m.p. 22°–22·5°; sp.gr. at 15°, 0·9144; acid number, 1·2; saponification number, 190·2; ether number, 189·0; iodine number, 72·1; Hehner's number, 95·16; Reichert-Meissl number, 0·4 (Kitt, Chem. Zeit. 1897, 21, 303).

Detection, estimation, and analysis.—The presence or absence of egg yolk in pastry can be determined by examination of the fat, there being a great difference in composition and properties between the fat of wheat and of the egg (Spaeth, Zeitsch. Nahr. Genussm. 1896, 10, 171). The amount of egg present in pastry, &c., may be determined by the amount of cholesterol present (Cappenberg, Chem. Zeit. 1909, 33, 985. (For methods for the determination of the constituents of egg yolk for commercial purposes, *see* J. Soc. Chem. Ind. 1906, 829.)

EGG ALBUMIN *v.* PROTEINS.

EGG FRUIT. The fruit of *Solanum melongena* (Linn.). A plant of tropical and sub-tropical countries. König gives, as the mean of three analyses—

Water	Nitrogenous matter	Fat	Soluble carbohydrates	Fibre	Ash
93·2	1·1	0·1	3·9	1·2	0·5

An American analysis (Bull. 28, U.S. Dept. of Agric.) shows a somewhat larger amount of carbohydrates (5·1 p.c.), but is similar in other respects.

This plant is sometimes called *Aubergine*. The fruit is used in much the same way as the tomato. H. I.

EGOLS. A class of antiseptics consisting of the potassium mercury salts of *o*-nitrophenolsulphonic acid, the individual members being termed 'phenegol,' 'cresegol,' &c., depending on the phenol from which they are derived. They are reddish-brown powders, readily soluble in water, and are strongly bactericidal (Gautrelet, Compt. rend. 129, [2] 113; J. Soc. Chem. Ind. 1899, 854) (*v.* SYNTHETIC DRUGS).

EGYPTIAN BLUE. This is a blue colouring matter which was used by the Romans in the first few centuries of the Chrisitian era, but ceased to be manufactured about the time of the invasion of the barbarians. It figures in several beautiful frescoes in the Vatican, and has also been found at Pompeii. Fouqué discovered the composition to be that of a double silicate of calcium and copper $CaO,CuO,4SiO_2$, devoid even of traces of alkali. The substance is crystalline, and is hardly attacked by any chemical reagents, which explains the perfect state of its preservation in the paintings for which it was employed 1900 years ago. It may be prepared at a bright-red heat, but this temperature must not be exceeded, as it is then decomposed into cuprous oxide, *wollastonite*, and a clear light-green glass. The higher the temperature, the more of the latter is formed, and, finally, wollastonite disappears entirely. By the old method of preparation, described by Vitruvius, fine sand and soda are intimately mixed with copper filings, then moistened with water, formed into cakes, and the latter dried. The cakes are then fused in an earthen pot until the blue colour is produced. Fouqué found this method practicable, but used potassium sulphate in preference to soda as a flux. It was not possible to replace chalk or lime by magnesia. The ancient Romans employed a large excess of silica, whilst Fouqué employed more basic mixtures, finally purifying the product with hydrochloric acid. The exquisite colour of this mineral body, the fact that it is absolutely unaffected by moisture, light, and most chemical reagents, as well as the facility and the low price of production, render it desirable that its manufacture should be again resumed (F. Fouqué, Compt. rend. 108, 325–327; and J. Soc. Chem. Ind. 8, 291).

EIKONOGEN. Sodium salt of 1-amino-β-naphthol-6-sulphonic acid. Used as a photographic developer.

EKSANTALAL $C_{12}H_{18}O$. Obtained on oxidation by ozone of the sesquiterpene primary alcohol α-santalol $C_{15}H_{24}O$, which, together with the isomeric β-santalol, constitutes 'santalol,' the oil resulting from the hydrolysis of the hydrogen phthalate made from the oil obtained by distilling sandalwood with steam (Semmler, Ber. 43, 1893).

It is dextro-rotatory (α_D +13·5°); b.p. 109°–110°, under 10 mm.; sp gr. 0·9846 at 20°/20°; n_D 1·48519.

It gives an oxime, which yields the corresponding nitrile and amine, and gives eksantalol on reduction (Semmler, Ber. 41, 1488).

Heated with acetic anhydride and sodium acetate, it forms *enol*-eksantalal acetate

$$C_{12}H_{17}O{\cdot}CO{\cdot}CH_3,$$

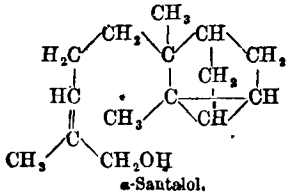
which, on oxidation with potassium permanganate, yields noreksantalic acid $C_{11}H_{16}O_2$ (Semmler, Ber. 43, 1722–1725), the methyl ester of which, on reduction by sodium and alcohol, yields noreksantalol $C_{11}H_{18}O$; and this on oxidation in benzene solution with potassium dichromate and dilute sulphuric acid, gives *noreksantalal* $C_{11}H_{16}O$, b.p. 92°–94°/11 mm.; sp. gr. 20°/20° 0·9964, n_D 1 48301, α_D −30·8°. The *enol*-noreksantalal acetate gives, on oxidation by potassium permanganate, *teresantalic* acid

$$C_{10}H_{14}O_2$$

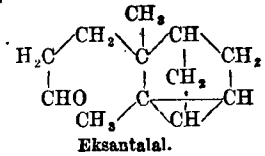
(Semmler and Zaar, Ber. 43, 1890).

In all three series, containing 10, 11, and 12 carbon atoms respectively, the same tricyclic system is present as exists in α-santalol; and

Semmler (Ber. 43, 1893–1898) assigns to these bodies constitutions based upon the camphene or camphor type, and α-santalol and eksantalal are structually represented as below:



α-Santalol.



Eksantalal.

EKTOGAN. Trade name for a mixture of zinc dioxide with zinc oxide and carbonate, used as a surgical dressing.

ELÆOMARGARIC ACID $C_{18}H_{32}O_2$. An acid, melting at 48°, obtained by the saponification of eläococoa oil (Japanese wood oil) with alcoholic potash, and decomposing the *trielæomargarin* thus formed. The glyceride when first formed is liquid, but on exposure to light gradually solidifies. Isomeric with eläostearic acid, eläoleic acid, and linoleic acid. On exposing an alcoholic solution to light, plates of eläostearic acid, m.p. 71°, are precipitated (Cloëz, Bull. Soc. chim. 1876, 26, 286; 1877, 28, 24); traces of iodine or sulphur also bring about this change (Maquenne, Compt. rend. 135, 696). Oxidation with potassium permanganate gives rise to azelaïc acid, sativic acid, and dihydroxystearic acid (Kametaka, J. Soc. Chem. Ind. 1903, 1138; 1908, 1120; Kit, Chem. Soc. Abstr. 1905, i. 10; Maquenne, *l.c.*). Linolic acid also on oxidation yields sativic acid, and on bromination, linolic acid and eläomargaric acid yield the same tetrabromide. Eläostearic acid and linoleic acid yield the same diozonide (Majima, Ber. 1909, 674). Eläomargaric acid and eläostearic acid are converted into eläoleic acid when heated at 180° in sealed tubes (Cloëz, J. 1878, 38).

ELÆOPTENE. The volatile portion of an essential oil, used in contradistinction to the *stearoptene* or solid portion.

ELAÏDIC ACID $C_{18}H_{34}O_2$. A solid stereoisomeric modification of oleic acid, obtained by the action of nitrous acid upon olive oil, saponifying the glyceride (elaïdin) so formed, and decomposing the salt by hydrochloric or sulphuric acid. May also be obtained by the action of nitrous acid or of nitric acid (sp.gr. 1·2) (Edmed, Chem. Soc. Proc. 1899, 190) upon oleic acid, or by decomposing barium oleate with fuming nitric acid; m.p. 52° (Saytzeff, Chem. Soc. Abst. 1893, 551); b.p. 287·5°–288° at 100 mm. (Krafft and Mördlinger, Ber. 1889, 819). Soluble in alcohol and ether. Solutions have an acid reaction. The melted acid gradually absorbs oxygen from the air, and becomes permanently liquid. It may be distilled unchanged under diminished pressure. Heated with potassium hydroxide, it is converted into acetate and palmitate of potassium with evolution of hydrogen.

Elaïdic acid dissolved in benzene, toluene, ligroïn, or chloroform, and mixed with caustic soda and shaken, gives a brilliant phosphorescence (Radziszewski, Annalen, 203, 305). Hydriodic acid forms an addition compound (iodostearic acid) with elaïdic acid (Farb. vorm. Fried. Bayer & Co. D. R. P. 180087; Chem. Soc. Abstr. 1907, i. 380), which, on treatment with alcoholic potash, yields oleic and *iso*-oleic acids (Lebedeff, *ibid.* 1893, 550). On reduction with nickel or copper and hydrogen at 280°–300°, elaïdic acid is converted into stearic acid (Sabatier and Mailhe, Ann. Chim. Phys. [8] 4, 319). Treated with dilute solution of potassium permanganate in presence of potash, it is converted into a dihydroxy acid, which differs from the corresponding compound obtained from oleic acid by its lower melting-point (99·5°), and its greater solubility in alcohol and ether, and also into pelargonic, azelaïc, and oxalic acids (Saytzeff, Ber. 1886, 21; Edmed, Chem. Soc. Trans. 1898, 627); oxidation with sulphuric acid, however, gives rise to the same dihydroxystearic acid as is obtained from oleic acid under the same conditions (Tscherbakoff and Saytzeff, J. pr. Chem. 1898, 27).

Elaïdin, a solid isomeride of olein, is obtained by the action of nitrous acid upon olein, and is probably a triglyceride $C_{57}H_{104}O_6$. It melts at 36°; is nearly insoluble in alcohol, readily soluble in ether. The *Unguentum oxygenatum* and *U. citrinum* of the pharmacopœias, prepared by the action of nitric acid upon hog's lard, contain impure elaïdin.

ELAÏDIN *v.* ELAÏDIC ACID.

ELALDEHYDE *v.* ALDEHYDE.

ELATERIN *v.* ELATERIUM.

ELATERITE. *Elastic bitumen, Mineral caoutchouc.* A fossil resin, somewhat resembling asphalt, found at Castleton in Derbyshire, in France, Switzerland, &c. It is a soft, flexible, elastic, and readily inflammable substance, with a resinous lustre and a dark-brown colour.

ELATERIUM. The sediment from the juice of the fruit of the *Ecbalium elaterium* (Richard), or squirting cucumber. Elaterium is a drastic purgative.

Pereira (Mat. Med. 3rd ed. 2, 1742) gives a *résumé* of the work of Braconnot, Clutterbuck, Paris, Marquart, and others on elaterium, and of the discovery of *elaterin* by Hennel (J. Roy. Inst. 1, 532), and independently by Morries (ed. Med. Surg. J. 35, 339; Annalen, 2, 366). Good specimens of elaterium when extracted with chloroform yield 25 p.c. of elaterin, which by recrystallisation is obtained in minute shining six-sided plates. The dose of elaterin is $\frac{1}{10}$ to $\frac{1}{5}$ of a grain, and to it is ascribed the whole of the physiological activity of elaterium. Elaterin is a neutral bitter compound, insoluble in water, but soluble in chloroform and hot alcohol. It melts at 200° (Zwenger, Annalen, 43, 360). If sulphuric acid be added to a solution of elaterin in melted phenol, a crimson colour is produced which changes to scarlet (Lindo, Chem. News, 37, 35; Johannson, Zeitsch. anal. Chem. 24, 154).

On hydrolysis with alcoholic potash, elaterin furnishes acetic acid and an amorphous compound, *elateridin*. Further action of alkali gives *elateric acid*, also amorphous, and melting at 73°–75° (Berg, Bull. Soc. chim. [iii.] 35, 435).

Elaterium of English origin, examined by Power and Moore (Pharm. J. [iv.] 29, 501), was found to contain 5·3 p.c. of moisture and 6·7 p.c. of ash. By a suitable method of extraction, a colourless crystalline product, m.p. 217°–220°, was obtained, corresponding with the elaterin of the pharmacopœias. This was found to be non-homogeneous, consisting of at least two substances, one, *α-elaterin*, melting at 230° with decomposition, and lævo-rotatory, whilst the other, *β-elaterin*, has a lower melting-point, and is dextro-rotatory. Both have the same empirical composition, but the former is physiologically inert, whilst the latter shows marked physiological activity. Examination of commercial elaterin showed that it consists mainly of varying proportions of these two substances, which probably accounts for the marked difference in medicinal value of different samples. α-Elaterin has also been found in colocynth, the dried fruit of *Citrullus colocynthis* (Schraeder) (Power and Moore, Chem. Soc. Trans. 97, 99), and has been further investigated by Moore (*ibid.* 97, 1797).

According to Berg (Bull. Soc. chim. [iii.] 17, 85; [iv.] 7, 385), elaterin does not exist ready-formed in the fruit, but is produced after the rupture of the tissues by the action of an enzyme *elaterase* on a glucoside present. The latter consists of a brittle, amorphous powder, and gives the same reactions as elaterin with sulphuric acid and phenol. Power and Moore (Chem. Soc. Trans. 95, 1985), however, on examination of the fresh fruit, failed to obtain any evidence of the presence of a glucoside of elaterin, but a small amount of an enzyme was found to be present. These investigators also obtained from the fresh fruit a small amount of a hydrocarbon, m.p. 68°, probably hentriacontane; a phytosterol $C_{27}H_{46}O$, m.p. 148°; a substance melting at 258°–260°, which appears to be related to ipuranol; a mixture of fatty acids and a product corresponding to the elaterin previously examined. A. S.

ELDERBERRY. The fruit of *Sambucus nigra* (Linn.). The only analysis quoted by König gives, as the composition of the fruit—

Water	Crude fibre	Pentosans
81·9	6·6	1·2

The berries are used for the preparation of a wine and of 'elderberry syrup,' an old-fashioned cordial. From the wine, a brandy is sometimes distilled, which according to analyses by Arnthor and Zink, quoted by König, contains 39·2 p.c. of alcohol (by weight) and has a sp.gr. of 0·836. According to de Sanctis (Gazz. chim. ital. 1895, 25, 49), elder leaves and stems contain conine. Malmejac (J. Pharm. Chim. 1901, 14, 17) attributes the diuretic and purgative action of the bark of the elder to an alkaloid, *sambucine*, a deliquescent bitter substance, yielding the usual alkaloid reactions. He also found elder bark to contain tannin, a resin resembling scammony and a yellowish-red oil possessing a strong odour of elder. Elder pith contains both xylan and araban (Browne and Tollens, Ber. 1902, 35, 1457). The oil extractable from the juice of red elderberries (*S. racemosa*) by ether, is light yellow in colour, has a sp.gr. of 0·9072, solidifies at −8°, and melts at 0°; contains 6·65 p.c. of free acid (as oleic acid), 0·66 p.c. of unsaponifiable matter, has a saponification number 209·3, iodine number 81·4, and Reichert-Meissl value of 1·54 (Byers and Hopkins, J. Amer. Chem. Soc. 1902, 24, 771).

The leaves of the elder contain a cyanogenetic glucoside, which, under the influence of emulsin, yields dextrose, benzaldehyde, and hydrogen cyanide; the yield of the last-mentioned amounts to 0·126 gram per kilogram of fresh leaves (Guignard, Compt. rend. 1905, 141, 16; Bourquelot and Danjon, *ibid.* 59). This glucoside, which has been named *sambunigrin* $C_{14}H_{17}O_6N$, crystallises from ethyl acetate in long, colourless needles, melting at 151°–152°, is readily soluble in water or alcohol, but nearly insoluble in ether (Bourquelot and Danjou, Compt. rend. 1905, 141, 598).

According to Ravenna and Tonegutti (Chem. Zentr. 1910, i. 544) the enzyme which decomposes the glucoside in the plant is not soluble in water. The hydrocyanic acid is present in larger quantities than has hitherto been believed, and is most abundant in the stalks. H. I.

ELECTRO-DEPOSITION and ELECTRO-PLATING. Electrolytic processes are now used to a considerable extent in the precipitation of metals in a reguline form, so as to be available for many commercial purposes. Thus the common and easily corroded metals are coated with thin films of electro-deposited metal of a more permanent and less oxidisable character, in the process of electroplating; for the reproduction of engraved surfaces, type, &c., in electro-deposited copper, electrolysis is applied in electrotyping; and in the deposition of a pure metal from an impure form or a mixture of metals, the principles of electrolysis are applied in the processes of electrolytic refining and in chemical analysis.

An electric current passed through solutions of metallic salts brings about decomposition of a particular type, and is accompanied by the deposition or evolution of the products, or others which may have been formed as the result of secondary changes. When copper sulphate solution is electrolysed with a platinum anode, copper is deposited at the cathode, and oxygen and sulphuric acid are formed at the anode, thus:

$$\underbrace{Cu}_{\text{Deposited on cathode.}} \leftarrow Cu\,SO_4 \rightarrow \underbrace{SO_4 + H_2O = H_2SO_4 + O}_{\text{Formed at anode}}$$

Other metallic compounds follow a similar course. The primary products of decomposition consist of charged atoms or groups of atoms. These are termed *ions*, and migrate to the electrodes, those to the anode being called the *anions*, and those to the cathode *cathions*. Anions consist of the acidic group of the salt, while the cathions comprise hydrogen, the metals, and basic radicles. At the electrodes, the electrical charges are neutralised, and the substance appears in the nascent form, subsequently being deposited or evolved. Elementary anions, such as chlorine, bromine, and iodine may enter into subsequent secondary changes, while others, such as NO_3, SO_4, $C_2H_3O_2$, &c., react with water, giving generally the corresponding acid, and liberating oxygen. With soluble anodes—those attacked by the anion—solution of the metal takes place, and thus, in a copper solution, a copper anode supplies metal under

the best conditions as rapidly as metal is deposited. The strength of the solution is thus maintained, a condition necessary for continuous deposition as required for plating and refining purposes.

The deposition of metals follows the usual law of chemical equivalents as enunciated by Faraday in 1835. The ampere-hour is thus associated with a definite amount of metal, which cannot be exceeded, but may not be attained owing to failure in realising the best conditions. The weights of metals deposited by the coulomb, ampere-hour, and 746 ampere-hours, are shown in the following table:

Metal	Chemical equivalent	Mgs. per coulomb	Grams per ampere-hour	Ozs. (av.) per 746 ampere-hours
Copper (cupric)	31·8	0·329	1·182	31·0
„ (cuprous)	63·6	0·658	2·364	62·0
Gold (auric)	65·7	0·680	2·440	58·6(Troy)
„ (aurous)	197·0	2·040	7·320	176·0 „
Iron	28·0	0·290	1·040	27·3
Lead	103·5	1·070	3·870	101·0
Nickel	29·3	0·302	1·085	28·5
Silver	108·0	1·118	4·025	96·5(Troy)
Tin (stannous)	59·0	0·610	2·190	57·5
„ (stannic)	29·5	0·305	1·095	28·7
Zinc	32·5	0·336	1·210	31·8

These amounts, however, can only be deposited when the cathode is surrounded by a considerable amount of strong electrolyte, and only under this condition can the facts of electrolysis be applied, as in the voltameter, to the determination of the number of coulombs passing through a circuit. While for most industrial purposes it is not necessary for the theoretical amount of metal to be deposited per ampere-hour, yet the most satisfactory deposits are, in many cases, obtained when this condition is most nearly attained. Failing the full amount of metal per ampere-hour, hydrogen is deposited, and this often leads to a dark powdery deposit unsuitable for industrial purposes. Such deposits, caused usually by excessive current, are said to be 'burnt.' In some solutions—for example, those of copper, iron, or nickel sulphate—this inferior deposit seems to result from the simultaneously deposited hydrogen due to a weak electrolyte. In other examples, that of the alkaline or cyanide copper bath, it would seem (from the fact that much hydrogen may be deposited without 'burning') more probably due to the deposition of traces of basic compounds with the metal (Bancroft, Trans. Amer. Electrochem. Soc. vi. [ii.] 27). This view is supported by the fact that the presence of substances in the solution, which are good solvents for such basic compounds, prevents 'burning' to a considerable extent. Thus, in the alkaline copper-bath, 'burning' is reduced, and the quality of the deposit improved by the addition of such salts as sodium bisulphite and potassium cyanide. In other examples, notably those of tin and lead, the deposit is much improved by the addition of a trace of a colloid, such as glue or gelatine.

Migration of ions. It is well known that ions migrate to their respective plates with definite speeds under unit potential gradient. If deposition proceeds more rapidly than this rate of migration, the cathode liquid becomes impoverished of its metal, and this involves a falling off in the ampere-hour yield. The deficiency of metal around the cathode is counteracted to a limited extent by the ordinary process of diffusion, but there is a limit at which metal may be satisfactorily deposited, unless special steps are taken to make up for this slow migration. Methods of circulation and stirring are based on this fact, and also on the further fact that the heavier solution formed around the anode falls to the bottom of the solution, and, owing to its superior conductance, gives rise to the conduction of an undue proportion of the current and consequently thicker deposits on the portion of the cathode in this heavier layer; hence a limit to the rate at which deposition may be safely allowed to proceed is set, and the time required to deposit a given amount of metal varies correspondingly.

E.M.F. for deposition. With an insoluble anode, a definite minimum E.M.F. is required to maintain electrolysis. Thus, when copper sulphate is decomposed with a platinum anode, the total change is as follows:—

$$CuSO_4 + H_2O = Cu + O + H_2SO_4.$$

This, as a chemical change, is endothermic, and electrolytically it demands a minimum E.M.F. of about 1·25 volts for its continuance. When a copper anode is used, no change in the composition of the solution occurs. Energy changes at both electrodes are equal and of opposite character, and hence a much smaller E.M.F., viz. that required to overcome the mere resistance of the solution, is required. With efficient anode solution and a good conducting electrolyte, such as is obtained in an acidified copper sulphate solution, a P.D. of about 0·3–0·5 volt will maintain a fair rate of deposition. In the case of nickel, where there is usually inefficient anode solution and a poorly conducting electrolyte, a much higher P.D. is required, partly on account of the greater stability of nickel compounds. Figures given, therefore, for P.D.'s at bath terminals are of a very elastic character, depending upon the efficiency of anode solution, strength of solution, temperature of the solution, distance between electrodes, presence or otherwise of conducting substances in the solution, and current density required; while the conditions controlling the allowable current density at the cathode are chiefly the strength of the electrolyte and its motion.

The **deposition of copper** may be accomplished by simple immersion methods, resulting in a chemical exchange with the more positive metal plated; thus:

$$\left.\begin{matrix}Zn\\Fe\end{matrix}\right\} + CuSO_4 = \left.\begin{matrix}Zn\\Fe\end{matrix}\right\} SO_4 + Cu.$$

The process is but little used, and then only for very cheap work. Deposits on a surface which is undergoing simultaneous corrosion, cannot be sufficiently adherent to withstand the frictional processes of polishing and burnishing.

The single-cell process, practised at one time, involves the generation of current and the deposition of metal in the same apparatus.

The process is illustrated in the Daniell cell, in which, if the copper cylinder is replaced by any conducting substance, copper is deposited.

For the deposition of copper on brass and similar electro-negative metals, and on black-leaded or metallised non-conducting surfaces of wax, guttapercha, plaster, earthenware, &c., the following solution is of wide application :—

Bluestone ($CuSO_4, 5H_2O$) . .	$1\frac{1}{2}$–2 lbs.
Oil of vitriol	$\frac{1}{4}$–$\frac{1}{2}$ lb.
Water	to 1 gallon

The composition is variable. Strong solutions admit of more rapid deposition without 'burning,' while the acid imparts conductance. From such a solution deposition can be carried on at the rate of 40 amperes per square foot without stirring, while, with a properly stirred electrolyte, this current density may be increased up to 250 or 300 amperes per square foot.

Previous to deposition, brass is cleaned first in potash (5–10 p.c.) to remove grease. It is then passed through aquafortis to remove scale of oxide, or tarnish, and, after rinsing, is scoured with pumice or ordinary sand or scratch-brushed. After finally rinsing, it is immersed in the solution, and should be covered immediately. The deposit is pink, though dull. When of sufficient thickness, the work is removed, rinsed, and the dull surface improved by scratch-brushing or polishing.

For deposition upon non-conducting substances such as wax, guttapercha, &c., the following methods may be used :—

(1) *Wax* and *guttapercha*. Thorough yet careful brushing with the finest plumbago causes sufficient to be retained to render the surface conductive. Such surfaces when suspended in the copper solution, receive a deposit beginning at the metal connection, and gradually spreading over the whole surface, the thickness of the deposit not being exactly uniform.

(2) *Plaster of Paris* and *unglazed earthenware* may be rendered conductive by first soaking in linseed oil and allowing to dry. They are thus rendered impervious to the solution, and the skin of dried oil will now retain blacklead, when this substance is applied by gentle brushing, sufficient to impart the necessary conductance.

(3) *Flowers, feathers,* and other delicate objects which will not withstand the pressure of even gentle brushing, may be treated to produce a fine layer of some metal or sulphide on the surface by simple chemical means. A usual method is to paint them or immerse them in a weak solution of phosphorus in carbon disulphide, and, after drying, a brief immersion in silver nitrate solution leads to the precipitation of silver, which imparts the necessary conductance. Again, the object to be treated may first be immersed in silver nitrate solution, and subsequently exposed to sulphuretted hydrogen, which produces a layer of silver sulphide, sufficient to cause the immediate deposition of copper at all points.

A more successful method for wax and guttapercha involves covering these substances with copper by simple precipitation. The substance, usually as a mould or impression of a surface to be reproduced in electrotype copper, is first blackleaded and is then laid face upwards in a solution of copper sulphate. Iron filings are then sprinkled on the surface. The filings in contact with the blackleaded surface produce innumerable voltaic couples, which bring about the deposition of copper quickly and completely. The mould is then rinsed to detach the filings, and placed in the bath, when copper is at once deposited uniformly over the whole surface.

On positive metals such as iron, zinc, tin, Britannia metal, pewter, &c., copper cannot be successfully deposited from the acid sulphate solution on account of the ease with which these metals turn out the copper by simple immersion, and are, moreover, corroded by the acid. A more stable and more satisfactory compound for this class of work is the double cyanide of copper and potassium (CuCN·KCN). Solutions of this compound are usually prepared by (1) dissolving the carbonate in a solution of potassium cyanide; (2) precipitating the sulphate with ammonia, dissolving the precipitate in excess of ammonia, and decolourising the blue solution with potassium cyanide. Many other methods are available and are in use. The strength of such solutions may be varied between wide limits up to 4 ozs. (or even more) of metal per gallon. An excess of potassium cyanide is essential, owing to the formation of insoluble single copper cyanide (CuCN) at the anode. The course of electrolysis in such double cyanide solutions (including those of zinc, silver, and gold) is very different from that of the salts of the mineral acids. In the case of copper, the reaction may be simply represented as follows :—

$$\text{Anode} \quad \leftarrow \quad \begin{matrix} CuCN\cdot KCN \\ Cu(CN)_2^{-}\cdot K^{+} \end{matrix} \quad \rightarrow \quad \text{Cathode}$$

then :

$$Cu(CN)_2 + Cu = 2CuCN. \quad \text{(insoluble)} \qquad K + CuCN\cdot KCN = Cu + 2KCN. \quad \text{(deposited)}$$

The copper in the salt thus migrates as a complex ion to the anode, and there forms an insoluble compound. This, unless removed, offers considerable resistance, and increases the difficulty of maintaining a normal current. Sufficient cyanide for its removal is formed at the cathode, and can be best brought to the anode by stirring, which facilitates the process of deposition by keeping the anode clean. The solution of the anode deposit is more usually accomplished by using an excess of cyanide called 'free cyanide.' From such a solution copper is not deposited upon iron, tin, Britannia metal, pewter, &c., by simple immersion, and only very slightly on zinc. The solution is conveniently used warm, and yields a deposit of copper accompanied by hydrogen, which, as a rule, does not seriously interfere with the physical character of the deposit. The deposit is, under the best qualitative conditions, smoother than that from the sulphate solution, and once the positive metal has been coated in this solution, it may be removed, and, after thorough rinsing, introduced into the sulphate solution for a thicker deposit. The cyanide solution, when strong, and used within a certain limit of current, yields twice as much copper per ampere-hour (viz. 2·36 grams) as the sulphate, the cyanide compound being a cuprous salt.

Applications of copper deposition.—The metal is most extensively deposited as a covering for

more positive and more corrodible metals, and as a preliminary deposit before coating with the more expensive metals. Deposits of copper on iron may then be burnished or polished and the surface improved by metal-colouring, when, by chemical processes, the surface is covered with a uniform film of oxide or sulphide by immersion in solutions producing these compounds, such as the salts of copper and soluble sulphides. Uniform and pleasing effects are readily obtained, and may be rendered more permanent by subsequent lacquering. The metal is also deposited on a considerable scale in the electrotyping process, thin, but rigid reproductions of type, engraved plates and blocks being made in electro-deposited copper, and subsequently strengthened by backing with a lead-antimony alloy, which is then planed down to the required thickness.

Analytically, copper deposition is applied in the separation of this metal from more positive metals in an acid solution with a platinum anode. From a solution of brass in nitric acid, the copper may be most completely deposited without interfering with the zinc. The copper deposit made on a platinum dish or suitable electrode is then weighed, and the zinc obtained by either a chemical or a further electrolytic method (*v.* ANALYSIS). On a commercial scale, the deposition of copper has been applied by Cowper-Coles to the production of parabolic mirrors for lighthouse work, and to the production of sheet, wire, and tubes. The manufacture of deposited tubes of large diameter has been successfully carried on by Elmore Bros., who arrange an agate burnisher to travel backwards and forwards along the tube during deposition, thereby producing a compact deposit of good mechanical properties. Tubes up to 16 feet long by 8 feet diameter, and weighing more than 3 tons, have been produced by this method. More usually, however, tubes are of smaller dimensions, and are subsequently drawn down or opened longitudinally for the production of sheets. Copper is deposited on a most extensive scale in the refining process, more than half a million tons of the metal annually being refined in this manner, using a solution of the sulphate with thick anodes of the crude metal. The crude metal contains up to 1·0 p.c. of impurities. The deposited metal is almost entirely free from impurity. Positive impurities pass into the solution, and are retained there by the application of the principle used in electrolytic analysis. Electro-negative impurities, as silver and gold, pass as chloride and metal respectively into the mud at the bottom of the tank, from which they may be recovered. Tin, antimony, arsenic, and bismuth are prevented from being deposited by a careful control of the conditions, and the sum-total of impurities in the refined metal is usually less than 0·05 p.c.

Deposition of silver. Silver, being an electro-negative metal, is readily deposited by simple immersion. The process is applied commercially under the name of 'whitening.' Solutions for this purpose contain a small proportion of a silver compound, such as chloride or cyanide, dissolved in cream of tartar, sodium chloride, or similar solvent. The deposition on properly prepared work is a case of simple replacement, and only very thin deposits are obtainable by this means. The same materials may also be used in the form of pastes, and rubbed on the prepared work with a wet rag, this method finding application in silvering clock and instrument dials.

Electro-deposition is most frequently practised. For this purpose the nitrate solution is unsuitable on account of its instability, being serviceable only as a voltameter electrolyte where the very electro-negative metal platinum is used. For silvering on more positive metals, those which usually require silver plating, a solution of the double cyanide of silver and potassium is used. This may be prepared from the metal as follows :—

(*a*) The metal is converted into nitrate, and precipitated with potassium cyanide. When precipitation is just complete, the clear liquid is decanted and the precipitate washed and subsequently dissolved in more cyanide solution, a further supply of cyanide being added for 'free cyanide.'

(*b*) Precipitation may be effected by common salt, and the washed chloride dissolved in excess of potassium cyanide.

(*c*) A silver plate may be made the anode in a 5 p.c. solution of potassium cyanide, using a small copper or carbon cathode contained in some of the solution in a porous cell. The silver dissolves electrolytically, and the process can be continued until sufficient silver has passed into the solution and a good deposit is obtainable from it.

The solution is used cold, and yields a dull deposit of the metal, which may subsequently be scratch-brushed, burnished, and polished. The addition of a small proportion of carbon disulphide (1 oz. in 250 gallons) completely alters the character of the deposit from dull to bright. 'Bright plating' is, therefore, much practised. The silver compound in the solution being somewhat unstable, special precautions are necessary before placing work in the solution for deposition. Copper, brass, and German silver may be plated directly, though previous to deposition it is common practice to pass such work through a solution of mercury cyanide. This solution can be prepared by treating a soluble mercuric compound with excess of potassium cyanide, or by dissolving the oxide in cyanide. A usual strength is 1 oz. of metal per gallon. From such a 'quicking' solution a bright deposit of mercury is obtained on brass, copper, and German silver by simple immersion, with the advantages that the more negative metal mercury is less oxidisable than copper, &c., and prevents simple immersion deposition of silver when the work is put into the bath, and possibly promotes the adhesion of the subsequently electrolytically deposited silver, by amalgamation. More positive metals, like iron and zinc, are first coppered in the alkaline bath, and subsequently treated as copper. With the lead alloys it is usual to pass them straight from the cleansing processes through a separate silver solution, from which a rapid deposit is first made. This, similarly with nickel, is termed 'striking,' after which the work is transferred to the main solution to complete the deposition.

The current density permissible is controlled largely by the metal content of the solution,

Excessive current produces a light-grey, dark-grey, or black deposit, which, being powdery, is unable to withstand the processes of burnishing and polishing.

Silver anodes should be of fine metal, preferably annealed, and, therefore, more susceptible to solution. Their behaviour is an indication of the condition of the solution. If a dull deposit collects upon them, with a falling off in the current, more free cyanide is required to dissolve the insoluble single cyanide which forms upon them. On the other hand, excessive free cyanide unduly promotes the solution of the anode, limits the permissible current density at the cathode, lowers the cathode efficiency, and promotes simple immersion deposition on work which is not 'quicked.' The amount of free cyanide present can easily be determined in this and other cyanide solutions with standard silver nitrate.

The deposition of gold is practised considerably on account of the pleasing colour and permanence of the deposit. Deposition is easy owing to the strong electro-negative character of the metal, and for electro-gilding, as with electro-silvering, cyanide solutions are used. Gold may be applied to metallic surfaces by three methods, viz.: (1) mercurial gilding; (2) simple immersion; and (3) the electrolytic method. Mercurial gilding is used for heavy deposits of gold. An amalgam of gold is first prepared by pouring mercury on to hot gold. Excess of mercury is squeezed through chamois leather, and the pasty amalgam preserved in balls under water. It is applied to the prepared metallic surface with a wire brush, which has first been wetted with a weak solution of mercuric nitrate. This is rubbed on the amalgam and then on to the work, depositing a layer of amalgam. When a uniform coating is obtained, the mercury is expelled in a muffle, and the process repeated for thicker deposits. The dull surface is improved by scratch-brushing. This process is largely employed.

Simple immersion methods are followed, for mere films of metal, in solutions of very varied composition. A moderately strong solution of sodium pyrophosphate is prepared (5–10 p.c.), and gold chloride added a little at a time. The warm solution at once gives up its metal, but the deposits can, in any case, only be very thin, though they may be thickened somewhat by 'quicking' in a mercury solution and reimmersing in the gold solution.

Gilding with the separate current is largely practised, using a solution prepared by the following or similar methods:—

(1) Making a gold sheet the anode in a cyanide solution (4 ozs. per gallon), using a cathode contained in a porous cell. The process is continued until sufficient metal is lost from the anode or until the solution yields a good deposit.

(2) Precipitating gold chloride with ammonia, avoiding excess, and dissolving the washed precipitate in potassium cyanide solution.

The metal content may vary from a few pennyweights to a few ounces per gallon. The solution is used warm with a gold anode, which is electrolytically corroded, or by a less desirable method of using an insoluble platinum anode and making frequent small additions of gold chloride. The colour of the deposit varies considerably with the conditions, chiefly that of current. Other conditions, such as temperature, size of anode, distance between electrodes, metal content, also apparently affect the colour; but these varying conditions primarily influence the current. Cold and weak solutions give a pale colour, which may be improved by warming. Excessive current produces darker and foxy deposits, which are, however, improved by scratch-brushing. More satisfactory deposition proceeds when the work is kept in motion. The colour of the deposit is heightened somewhat by a preliminary coating of copper, while a deposit of silver has the reverse effect, though occasionally required. The colour is modified also by the addition of copper and silver cyanides to the solution. Thick deposits are most satisfactorily obtained by occasional scratch-brushing and 'quicking.'

The deposition of nickel is now very largely applied on account of the hardness of the deposit and its permanence, together with the exceptional lustre which can be imparted to it by polishing. The solution most commonly employed is:

Nickel ammonium sulphate	12 ozs.
Water	1 gallon.

To this solution, additions are frequently made to increase the conductance, sal-ammoniac or common salt being used. Owing to the fact that no free mineral acid is permissible, and the tendency also to the formation of nickel hydroxide at the cathode, small additions of acids, such as citric, boric, or acetic, are made with varying success. The only modification in the above solution which adds any appreciable advantage, is that of nickel sulphate, which is so much more soluble than the double salt, and from which, therefore, much stronger and therefore better, conducting solutions can be prepared. For thick deposits, Langbein recommends the use of 3 lbs. of nickel sulphate per gallon, with the addition of ethyl sulphate or magnesium ethyl sulphate. On account of the greater stability of nickel compounds and the poor solution of the anodes, and also the absence of free mineral acid, a distinctly higher E.M.F. is required than for copper deposition, viz. 5–6 volts for 'striking,' that is, rapidly coating the work with nickel, and then 2–3 volts for depositing the bulk of the metal. The absence of free acid necessitates especial care in the preliminary cleansing processes, most work being finally passed through a weak solution of cyanide (5 p.c.), and quickly and thoroughly rinsed before being put into the vat. The nickel-plating solution is usually worked cold, and is conveniently contained in lead-lined vats. Anodes may be of cast or rolled metal, the cast being much superior, as its porosity assists its corrosion under the influence of the current. Rolled metal is but little attacked by the anion SO_4, and, failing the solution of the anode, sulphuric acid is produced and oxygen evolved; thus:

$$SO_4 + H_2O = H_2SO_4 + O.$$

This acidity is to be avoided, and with it there is a diminution in the metal content of the solution which is similarly undesirable.

Cast anodes are therefore much more largely used, more uniform conditions being maintained with them. On account of the high E.M.F. used, some hydrogen is evolved at the cathode, though the current efficiency should not ordinarily fall below 90 p.c. Occasional motion of the work is desirable in order to disengage any bubbles which may collect. Once deposition has commenced, the work should not be exposed more than momentarily, otherwise an imperceptibly thin film of oxide will form and almost entirely prevent the adhesion of further deposited metal. In fact, it is considered impossible to successfully deposit nickel on such a surface or on a previous deposit. On this account, previously nickelled work should be entirely freed from its nickel, and, while this may be done by acid solutions, common practice follows the method of polishing, at the same time preparing the surface for the new deposit. Copper and brass work is nickelled directly after the usual cleaning operations, whilst positive metals like zinc and Britannia metal require a previous deposit of copper from the cyanide bath. Iron and steel may be nickelled without coppering, the polished surface being first rendered somewhat dull by scouring with finest pumice. The deposit should be kept bright, and this is attained by a current density not exceeding 5 amperes per square foot. Higher current densities produce dull deposits, tending to become powdery on the edges. The nickel deposit is very hard, and the final lustre is obtained by 'finishing' with Sheffield lime, which produces a highly lustrous surface. In addition to the extensive cycle and motor industry, nickel-plating is applied considerably for small machine parts and instrument work and for 'facing' stereotypes, the deposit being much more durable than the stereotype metal.

The **deposition of iron** is carried out on lines similar to those for nickel, solutions of ferrous sulphate or ferrous ammonium sulphate being used. These must be entirely free from mineral acid, more so than in the case of nickel, and water should be well boiled before being used, to expel air and prevent the oxidation of ferrous to ferric compounds. Ferric compounds under electrolysis yield little metal, being reduced to ferrous at the cathode. The process is not much used beyond the application in 'steel-facing' engraved plates. The iron deposit obtained is free from carbon, but is very hard. Anodes of the softest wrought iron containing a minimum of carbon are desirable, and require occasional scouring to remove the layer of insoluble carbon. The deposition of iron has also been used for thicker deposits, which have subsequently been removed and examined to investigate the properties of pure iron, and to more successfully determine the effect of impurities. For 'steel facing,' the engraved plates are cleaned, any scouring being done with only a light brush. The plate is then hung in the bath and covered quickly by 'striking.' Deposition is then continued more slowly for 10–15 minutes. The deposit is very hard and withstands the printing process much better than copper. When the deposit shows signs of wear by the exposure of copper, the metal is simply and readily removed by immersion for a short time in a 5–10 p.c. sulphuric acid. By voltaic action the iron is soon dissolved from the plate, and, after a light scouring with a fibre brush and subsequent rinsing, the plate is again immersed in the solution to receive a further coating of iron, thus considerably lengthening its life.

Deposition of alloys. (1) *Brass.* From mixed solutions of zinc and copper sulphates with the addition of acid, copper can be completely deposited free from zinc, this principle being applied in electrolytic analysis and also in refining. With salts more alike in stability, the two metals are deposited simultaneously in proportions varying with conditions. The cyanides are invariably used for this purpose, the zinc and copper compounds being used in about the same quantity. The mixed solution may be prepared in many ways, of which the following are in common use:—

(*a*) Treating solutions of the mixed sulphates with excess of ammonia and adding about 30 p.c. more cyanide (KCN) than is required to decolourise the blue solution.

(*b*) Preparing a solution of potassium cyanide (1–1½ lbs. per gallon) and saturating about three quarters of it with the mixed carbonates of zinc and copper, subsequently adding the remaining solution for 'free cyanide.'

The solution may be used warm or cold. If cold, a higher concentration is desirable, and also a smaller proportion of zinc compound. If warm, the zinc compound should be increased and the solution may be safely diluted. Brass anodes are used, and, in a warm solution with a fair proportion of free cyanide, dissolve under the influence of the current. Lack of free cyanide gives rise to the formation of a deposit of the two single compounds on the anode, adding resistance and reducing the current, and thus altering the colour of the deposit. The colour and composition of the deposit vary with several conditions. In general, the conditions which demand a higher E.M.F. give rise to a lighter deposit containing more zinc, whilst those which reduce the resistance of the solution tend to the production of redder deposits containing more copper. Thus yellower deposits are produced in cold dilute solutions with little free cyanide, whilst the copper in the deposit is increased when the solution is strengthened or warmed, or more free KCN added. The composition of the deposit is controlled also by the proportion of the two metals in the solution, and the fact that from cyanide solutions copper and zinc are ordinarily deposited in the proportion of 63·6 of copper: 32·5 of zinc accounts approximately for the 2:1 proportion in deposited yellow brass. The colour of the deposit is lightened by the addition of ammonia or ammonium carbonate, these substances assisting the solution of the zinc compound, which is less soluble than the copper compound, and preventing the formation of basic compounds.

The methods of deposition of brass follow on the same lines as those of copper from the cyanide solution.

(2) Other alloys are deposited to only a very limited extent. The choice of solutions depends upon the ease of mixture of solutions from which the constituents can be separately deposited. Thus for bronze, the sulphate, chloride and cyanide solutions, are unsuitable.

A satisfactory mixture can be made from the double oxalates of the two metals with ammonium oxalate, the solution being worked warm with a bronze anode. Similarly, a solution from which German silver may be deposited may be prepared by mixing the separate double cyanides of copper, zinc, and nickel with potassium cyanide, or by dissolving the alloy in nitric acid, precipitating the mixed carbonates and dissolving the mixture in cyanide. The deposition of these alloys is subject to the same conditions as for brass, attention being paid to those conditions which facilitate the deposition of the more positive constituents, viz. tin, zinc, and nickel.

Deposition of tin may be successfully carried out from a number of solutions. The chloride yields a beautiful crystalline deposit, but reguline deposits may be obtained from solutions of the stannite, stannate, or double oxalate with ammonium, with ease. They are prepared as follows :—

(1) The hydrate is precipitated from stannous chloride with alkali, and the precipitate dissolved in excess of alkali.

(2) By converting the metal to hydrated oxide with nitric acid, and dissolving the washed oxide in alkali.

(3) By adding a solution of ammonium oxalate to tin chloride. A white precipitate first forms, and this is soluble in excess.

Solutions containing from 1 to 2 ozs. of metal per gallon are of convenient strength. From these solutions tin may be obtained as a reguline deposit within certain limits of current density. Excessive current produces a grey spongy deposit, which may, however, be considerably improved by the addition of a small amount of glue or gelatine, thereby extending the limit of allowable current. Solutions of moderate strength yield metal quantitatively, and the anode suffers normal corrosion, maintaining the strength of the electrolyte. The dull white deposit is improved by gentle scratch-brushing with a soft brush. Tin may also be deposited without the current by using an oxalic acid solution to which tin chloride is added. The metal is deposited by simple immersion, and the process may be improved by the addition of grain tin with the work, which facilitates deposition by local voltaic action, while tin passes into the solution. The process is hastened by immersing the small work in zinc trays, the zinc passing into the solution as an anode. In this case the solution must be replenished with tin chloride, and rejected when any large amount of zinc has accumulated in it.

The **deposition of lead** may be similarly effected from alkaline solutions, which yield reguline deposits, whilst the acetate produces the well-known crystalline deposit. The process has but little application, but more recently the deposition of the metal has been successfully applied by Betts to the refining of the metal. The electrolyte is a solution of lead fluosilicate, which may be made by dissolving the oxide or carbonate in the acid. With unrefined anodes the lead passes into solution, whilst silver is retained in the anode mud. Good reguline deposits are obtained by the addition of glue or gelatine in small amount.

A feature of lead deposition is the production of lead peroxide at the anode. This has long been known, and the production of coloured rings and films was first observed by Nobili, in 1826. Thus in a solution of lead acetate, or of litharge in alkali, and a polished anode of nickel or iron, coloured rings are obtained if a wire cathode is held close to the anode. The colours are due to the gradually varying thickness of the film, which brings about interference in the light falling upon them. With anodes of other shapes the colours follow the shape of the anode, though they pass off into a more or less rounded form. These colours are called 'metallochromes.' With excessive current a dull-brown deposit of lead peroxide is at once formed.

The **deposition of platinum** is carried out from a solution of the chloride in sodium phosphate. A platinum anode is insoluble and the solution needs the addition of the platinum compound. A brown colour sometimes occurs owing to some of the metal passing into the colloidal form.

Palladium may be successfully deposited from a solution of its double chloride, and the process has been applied by Cowper-Coles for producing a non-corrodible covering for electrolytically deposited parabolic mirrors in copper.

Cobalt deposition follows on lines similar to those for nickel, whilst **mercury**, which may be deposited from the nitrate solution, has been applied to the construction of electrolytic meters, in which a small and definite fraction of the total current is shunted through a cell in which mercury is deposited, the weight of the mercury deposit automatically recording the current passing through the meter, and at constant potential difference the energy absorbed in the circuit. S. F.

ELEMI *v.* OLEO-RESINS.

ELEMI, ESSENTIAL OILS OF, *v.* OLEO-RESINS.

ELIQUATION or **LIQUATION.** A metallurgical term to denote the operation of separating substances by taking advantage of their different fusibilities.

ELLAGIC ACID. Ellagic acid $C_{14}H_6O_8$ is obtained from numerous tannin matters which contain an ellagitannin (*see* art. on TANNIN) by boiling the aqueous extract with dilute sulphuric acid. In many cases it is to be found in the free state, due probably to the hydrolysis, by fermentation, of the ellagitannin or ellagic acid glucoside originally present, and such a fermentation frequently occurs when aqueous extracts of the tannin matters are allowed to stand for some time.

Divi-divi (*Cæsalpinia coriaria* [Willd.]) (Löwe, Fresenius Zeitsch. anal. Chem. 1876, 14, 40), myrabolans (*Terminalia chebula* [Ratz.]) (Löwe, *ibid.*), algarobilla (*Cæsalpinia brevifolia*) (Zölffel, Beilstein, 2, 1085), and valonia (*Quercus Aegilops* [Linn.]) yield considerable quantities of ellagic acid, and are the best natural sources of this material. It has also been isolated from oak galls (Chevreul, Ann. Chim. Phys. 1828, [2] 9, 329); oak bark (Etti, Montash. 1880, 1, 226); the bark of *Picea excelsa* (Link.) (Strohmer, *ibid.* 1881, 2, 539); pomegranate rind (Rembold, Annalen, 1867, 143, 288); *Quebracho colorado* (Perkin and Gunnel, Chem. Soc. Trans. 1896, 69, 1307); *Arctostaphylos Uva-ursi* (Spreng.) and *Coriaria myrtifolia* (Linn.) (Perkin, *ibid.* 1900, 77, 424); *Hæmatoxylon campeachianum* (Linn.)

(Perkin, *ibid.* 1897, 71, 1137); the fruit of *Cæsalpinia digyna* (Rottl.) (Nierenstein, Chem. Zeit. 1909, 87); and the bark of *Terminalia Catappa* (Linn.) (*ibid.*). In fact, ellagic acid probably always occurs, if only in minute quantity, in all plant products which contain gallotannin. Most interesting are the Oriental bezoar *stones*, concretions which are found in the stomachs of goats and other animals, and consist largely of ellagic acid. These originate, without doubt, from the fact that the animal has fed upon plants in which some quantity of an ellagitannin is present.

Ellagic acid was first discovered by Chevreul (Ann. Chim. Phys. *l.c.*) in oak galls, and more closely examined by Braconnot (*ibid.* 9, 187). According to Pélouze, it possesses the composition $C_7H_4O_4$ (*ibid.* 54, 356); whereas Merklein and Wöhler (Ann. Chem. Pharm. 55, 129), who isolated it from bezoar stones and termed it 'bezoaric acid,' showed that its formula is $C_{14}H_8O_8$.

The precipitate of crude ellagic acid, which is produced by boiling the tannin extract with dilute acid, is purified by washing with alcohol and subsequent recrystallisation. A similar procedure is also satisfactory with the deposits so frequently produced by fermentation and alluded to above. Ellagic acid is most readily crystallised from pyridine (Perkin and Nierenstein, Chem. Soc. Trans. 87, 1416), and the product, which contains pyridine of crystallisation, is washed with alcohol.

Löwe (Zeitsch. Chem., 1868, 4, 653) was the first to prepare ellagic acid synthetically by oxidising gallic acid with arsenic acid, and this was subsequently accomplished by Ernst and Zwenger (Annalen, 1871, 159, 32) by heating the acid ethyl gallate with sodium carbonate solution in the presence of air, and by Griessmayer (Annalen, 1871, 160, 55) by heating gallic acid with water and iodine. It is readily produced by oxidising gallic acid dissolved in acetic acid by means of potassium persulphate and sulphuric acid (Perkin and Nierenstein, *l.c.*), and together with flavellagic acid by the addition of potassium persulphate to a solution of gallic acid in sulphuric acid (Perkin, *ibid.* 1906, 89, 251). Under similar conditions, gallotannin produces ellagic acid (Nierenstein, Ber. 1908, 41, 3015; and 1909, 42, 353), and it can also be prepared by boiling the tannin with hydrogen peroxide solution (*ibid.* 1907, 40, 917). Herzig and Bronneck obtained good results by passing air through an ammoniacal solution of gallic acid, and also of gallotannin (Montash. 1908, 29); whereas Sisley (Bull. Soc. chim. 1909, [4] 5, 727) prepared ellagic acid from tannin by means of alcoholic potassium hydroxide solution. According to Rupe, a 60 p.c. yield is produced when gallic acid in sulphuric acid solution is oxidised with sodium nitrite (Chemie d. naturl. Farbstoffe, 1909, 2, 162).

Ellagic acid crystallised from pyridine forms prismatic needles, which are converted by alcohol into a pale-yellow crystalline powder; but when purified by means of its acetyl- derivative, the product is almost colourless (P. and N.). It is very sparingly soluble in all the usual solvents, dissolves in alkaline solutions with a pale-yellow colour, and from these liquids, when diluted with hot alcohol, is deposited on acidifying in a crystalline condition. When heated, it does not melt below 360°; and sublimes at higher temperatures with considerable carbonisation. With nitric acid containing nitrous acid and subsequent dilution, it gives a blood-red colouration (Griessmayer's reaction), and this reaction, considered to be characteristic, is known to be also possessed by flavellagic acid (P.).

According to Merklein and Wöhler (*l.c.*), the alkaline solution of ellagic acid becomes reddish-yellow on exposure to air, and deposits black crystals of *potassium glaucomelanate* $K_2C_{12}H_{14}O_7$. When boiled with phenylhydrazine in alcoholic solution, or when carefully heated with phenylhydrazine, ellagic acid forms the product $C_6H_5NH\cdot NH_2,C_{14}H_6O_8$, which crystallises in yellow needles, and is readily reconverted into ellagic acid. Ellagic acid gives similar compounds with aniline and quinoline (Goldschmidt, Monatsh. 1905, 26, 1139).

Tetraacetylellagic acid $C_{14}H_2O_8(C_2H_3O)_4$ (Barth and Goldschmidt, Ber. 1878, 11, 846; Schiff, *ibid.* 1879, 12, 1534; Zölffel, Arch. Pharm. 229, 123), colourless needles, m.p. 343°–346° (Perkin and Nierenstein); *tetrabenzoylellagic acid* $C_{14}H_2O_8(C_7H_5O)_4$, colourless needles (Goldschmidt and Jahoda, Monatsh. 1892, 13, 151), m.p. 332°–333° (Perkin); *ellagic acid monomethyl ether* $C_{14}H_5O_7(OCH_3)$, yellow crystalline powder (Goldschmidt, Monatsh. 1905, 26, 1139); *diacetylellagic acid monomethyl ether*

$$C_{14}H_3O_7(OCH_3)(C_2H_3O)_2,$$

crystalline powder (G.); *ellagic acid dimethyl ether* $C_{14}H_4O_6(OCH_3)_2$, crystalline powder (G.); and *ellagic acid tetramethyl ether* $C_{14}H_2O_4(OCH_3)_4$, colourless microscopic needles (G.; Herzig and Polak, Monatsh. 1908, 29, 263), have been described.

Ellagic acid gives the following salts: $KC_{14}H_5O_8$, minute yellow needles (Perkin and Wilson, Chem. Soc. Trans. 1903, 83, 134); $K_2C_{14}H_4O_8$, prisms (Merklein and Wöhler; P. and W.); $K_2C_{14}H_4O_8,KOH$, microscopic prisms (M. and W.); $Na_2C_{14}H_4O_8$, crystalline powder; $NaC_{14}H_5O_8,H_2O$, yellow needles (Ernst and Zwenger, Annalen, 1871, 159, 32).

The tinctorial properties of ellagic acid are somewhat feeble, but in 1887 it was placed on the market by Messrs. Meister, Lucius, and Brüning, under the name of 'Alizarin Yellow in paste,' and was recommended as yielding, with chromium mordants, greenish-yellow shades of considerable permanence.

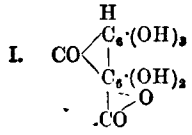
Rembold (Annalen, 1867, 143, 288) states that when ellagic acid is treated with sodium amalgam, it gives *γ-hexahydroxydiphenyl*

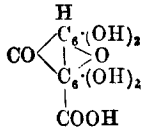
$$C_{12}H_4(OH)_6,$$

three distinct *rufohydrocellagic* acids, $C_{14}H_{10}O_8$, $C_{14}H_{10}O_7$, $C_{14}H_{10}O_9$, and *glaucohydrocellagic acid*; but, according to Nierenstein (Ber. 1908, 41, 1649), this latter compound is in reality the pentahydroxydiphenylmethylolid referred to later. By the action of boiling potassium hydroxide solution (Barth and Goldschmidt, Ber. 1879, 12, 1242), ellagic acid gives *hexahydroxydiphenyleneketone* (?) $C_{13}H_8O_7$, by fusion with potassium hydroxide *β-hexahydroxydiphenyl*, and by fusion with sodium hydroxide *γ-hexahydroxydiphenyl*, together with some of the *β-* compound.

When ellagic acid is distilled with zinc-dust fluorene is produced (Rembold, Ber. 8, 1494; Barth and Goldschmidt, *ibid.* 11, 846; *cf.* also Graebe, *ibid.* 1903, 36, 212).

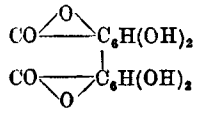
As a result of their investigation, Barth and Goldschmidt (*ibid.* 1879, 12, 153) suggested that ellagic acid could be represented by one of the two following formulæ:—

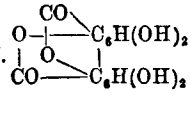
I. 

II. 

and of these the first was preferable.

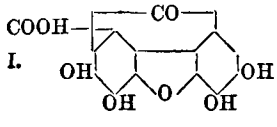
Whereas such a constitution requires the presence of five hydroxyl- groups, Schiff (Ber. 1879, 12, 1534) considered that acetylellagic acid was $C_{14}H_2(C_2H_3O)_4O_8$, and this was subsequently corroborated by Zölffel (Arch. Pharm. 229, 123). Schiff, at the same time, proposed two formulæ for ellagic acid:

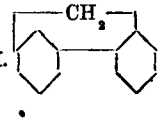
I. 

II. 

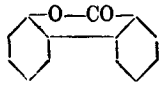
the latter of which is identical with that preferred by Graebe (*l.c.*). In a later investigation, Goldschmidt and Jahoda (Monatsh. 13, 49), as the result of their preparation of a tetrabenzoyl ellagic acid, were satisfied of the existence in ellagic acid of but four hydroxyls, and consequently adopted their second formula.

Graebe (Ber. 1903, 36, 314), among other criticisms, pointed out that a substance having this constitution, and which may be more clearly written as follows (I.):—

I. 

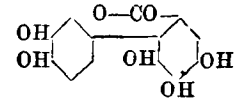
II. 

would yield, on distillation with zinc-dust, not fluorene, but an isomeric hydrocarbon (II.), if this, indeed, were capable of existence. In the same paper this author announced the interesting fact that diphenylmethylolid

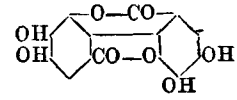


on distillation with zinc-dust, gives not only diphenyl and methyldiphenyl, but also fluorene; and in a theoretical discussion of the subject, suggested that Schiff's second formula (given above) most probably represents the true constitution of this substance.

The subject was reinvestigated somewhat later by Perkin and Nierenstein (*l.c.*), who, on digesting ellagic acid with boiling potassium hydroxide solution, obtained Barth and Goldschmidt's so-called hexahydroxydiphenyleneketone $C_{13}H_8O_7$. From this substance a *penta-acetyl* derivative $C_{13}H_3O_7(C_2H_3O)_5$, prismatic needles, m.p. 224°–226°, and a pentabenzoyl derivative, $C_{13}H_3O_7(C_7H_5O)_5$, plates, m.p. 257°–259°, were prepared. As, moreover, zinc-dust distillation gave fluorene, there could be little doubt that this compound was in reality *pentahydroxydiphenylmethylolid*, as, indeed, was surmised by Graebe:



From their results, together with a study of other similar compounds, Perkin and Nierenstein considered that Schiff's formula, also advocated by Graebe, and which can be more clearly written thus:



is a correct representation of the constitution of ellagic acid.

These authors have also prepared from *m*-hydroxybenzoic acid, *p*-hydroxybenzoic acid, protocatechuic acid; and from ellagic acid itself, other members of this group:

Metellagic acid $C_{14}H_5O_4(OH)$, (P. and N.)

Catellagic acid $C_{14}H_4O_4(OH)_2$, (P. and N.)(*see also* Schiff, Ber. 1882, 15, 2570).

Flavellagic acid $C_{14}HO_4(OH)_5$, (P.)(Chem. Soc. Trans. 1906, 89, 251).

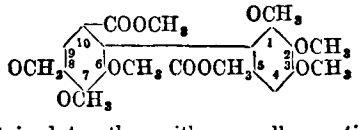
Cæruleoellagic acid $C_{14}O_4(OH)_6$, (P.) (Chem. Soc. Proc. 1906, 22, 114).

The two latter compounds are possessed of well-marked dyeing properties.

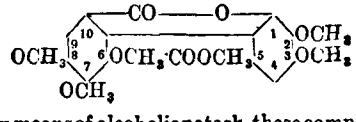
Herzig and Tscherne also include resoflavine $C_{14}H_3O_4(OH)_3$ from sym. dihydroxybenzoic acid in this group (Annalen. 351, 24).

Finally, Herzig and Polak (Monatsh. 1908, 29, 263), by a study of the methylation products of ellagic acid, have given a further corroboration of its constitution.

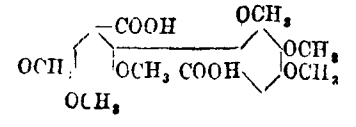
When Goldschmidt's tetramethylellagic acid is digested with alcoholic potash and methyl iodide *diphenyl*-1:2:3:6:7:8-*hexamethoxy*-5:10-*dicarboxylic methyl ester* (m.p. 109°–111°):

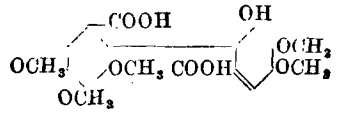
I. 

is obtained, together with a small quantity of *diphenylmethylolid*-2:3:6:7:8-*pentamethoxy*-5-*carboxylic acid methyl ester* (II.), m.p. 187°–189°:

II. 

By means of alcoholic potash, these compounds I. and II. yield respectively *diphenyl*-1:2:3:6:7:8-*hexamethoxy*-5:10-*dicarboxylic acid* (III.), m.p. 238°–240° and *diphenyl*-2:3:6:7:8-*pentamethoxy*-1-*hydroxy*-5:10-*dicarboxylic acid* (IV.), m.p. 200°–203°:

III. 

IV. 

Ellagic acid is probably not a tanning matter in the true sense of the word, but is of considerable importance nevertheless in the tanning process. Thus the ellagitannic acid absorbed by the hide is at least in part converted into ellagic acid, and the deposit thus formed adds weight and bloom to the finished article.

A. G. P.

ELLAGITANNIC ACID. A tanning principle present in divi-divi (Löwe, Frdl. 14, 35); in algarobilla (Zölffel, Arch. Pharm. 229, 123); in myrobalans (Löwe, *l.c.* 44; Zölffel, *l.c.*); and probably to some extent in all plant products which contain a gallotannin (*v.* ELLAGIC ACID).

According to Löwe, the molecule of ellagitannic acid contains 5 hydroxyl groups replaced by acetyl. It gives precipitates with gelatin, albumen, alkaloids, tartar emetic, and a nearly black precipitate with ferric acetate. Its alcoholic solution gives, with lead acetate, a precipitate of the formula $2C_{14}H_{10}O_{10}\cdot 5PbO$.

Very little is known of its constitution. Zölffel (*l.c.*) considers it a sugar-free tannic acid of the formula $C_6H_2(OH)_2COO\cdot C_6H_2(OH)_2COOH$. Perkin and Nierenstein (*l.c.*) consider it a glucoside of gallotannin or a condensation of two molecules of the latter, and suggest a constitutional formula.

Nierenstein (Ber. 1910, 43, 1267) has obtained it in a pure state by repeated treatment of the crude substance from myrobalans with alkali and ethyl chloroformate, and then decomposing with pyridine according to Fischer's method; and gives its formula as

$$C_{28}H_{28}O_{19},3H_2O.$$

It crystallises from a mixture of pyridine and acetic acid in pale-yellow plates, which, after sintering at 300°–306°, melt at 329°–336° $[\alpha]_D^{17}+18°02$. So obtained, it readily yields ellagic acid with dilute sulphuric acid, but is not decomposed by 10 p.c. sodium carbonate solution. As it is hydrolysed by emulsin to luteo-acid, Nierenstein considers it to be a glucoside of luteo-acid (*v.* TANNINS).

ELUTRIATION. The separation of the lighter from the heavier particles of a powder by washing and decantation.

EMANIUM *v.* ACTINIUM.

EMBOLITE. Native silver chlorobromide containing chlorine and bromine in indefinite proportions. It is the commonest of the horn-silvers or cerargyrites (*q.v.*), occurring as compact horn-like masses or as small, indistinct cubic crystals of a greenish-grey colour. Frequently a small amount of iodine is also present, and the formula is Ag(Cl,Br,I); the colour is then usually greenish-yellow to orange-yellow. Large quantities have been mined with other ores of silver in Chile, Mexico, and Broken Hill in New South Wales (*v.* Prior and Spencer, Min. Mag. 1902, 13, 174). L. J. S.

EMERALD *v.* BERYL, and GLUCINUM.

EMERALD GREEN. *Hydrated chromium sesquioxide* (*v.* CHROMIUM); also applied to *Schweinfürth green* (*v.* art. ARSENIC; also PIGMENTS).

EMERALD, ORIENTAL, *v.* CORUNDUM.

EMERY. (*Smirgel*, Ger.) An impure variety of corundum. Microscopic examination shows that it is a mechanical aggregate of crystalline or granular corundum and oxide of iron, chiefly in the form of magnetite, together with smaller amounts of several other minerals, such as tourmaline, hercynite ($FeAl_2O_4$), garnet, muscovite, diaspore, kyanite, rutile, &c. It was formerly obtained almost exclusively from Naxos, an island in the Greek archipelago, where it is found in large detached blocks in the soil, and also embedded in crystalline limestone. In consequence of deficient harbour accommodation, it is generally taken to the neighbouring island of Syra, and thence re-shipped. The lessee is bound by the Greek Government to extract a minimum of 1650 tons annually. The amount exported from Syra in 1907 was 10,982 tons, valued at 45,505*l*. In France, the Naxos emery is still used to the exclusion of most other kinds, but in many markets the Greek emery has been largely displaced by the Turkish.

J. Lawrence Smith first called attention to the occurrence of emery in Asia Minor, especially at Gumach Dagh, a mountain about 12 miles east of Ephesus. It is also found near Kulah, 20 miles from Philadelphia. The Thyra mines are situated in the hills between Cosbunar and Thyra; and at the foot of this range is the Coursack mine, where a large bed of emery is now worked. At some of these localities the emery is found as loose blocks in a reddish soil, but at most of the workings it is now systematically mined by shafts and galleries. The principal workmen are Italians. The large blocks of emery are broken by sledge-hammers, but as the mineral is extremely tough, it is often exposed to the action of fire and then cooled, to facilitate fracture. The broken emery is carefully picked over by hand, and sometimes not more than half is worth sending away. It is removed on camels and donkeys to the Ottoman Railway, and thence conveyed to Smyrna. From this port 28,559 tons were shipped in 1907. The only other emery-producing country is the United States, where it is mined at Chester in Massachusetts, and at Peekskill in Westchester Co., New York. The production in 1907 amounted to 970 metric tons, valued at 2524*l*.

Emery is extensively employed in a variety of ways as an abrading agent. The mineral is crushed, sifted through wire sieves, and sorted into different degrees of fineness, known as coarse, fine, and flour; and should then be washed and elutriated. Lawrence Smith found that the effective hardness, or abrading power, is not in direct proportion to the amount of aluminia in the emery, but seems rather to depend on the state of aggregation of the mineral. The following analyses are by Lawrence Smith (Amer. J. Sci. 1851, 11, 366). The first column gives the effective hardness, taking that of sapphire as 100 (*v.* CORUNDUM):—

——	Hardness	Sp. gr.	Al_2O_3	Fe_3O_4	SiO_2	CaO	H_2O
Gumach . .	47	3·82	77·82	8·62	8·13	1·80	3·11
Naxos . . .	46	3·75	68·53	24·10	3·10	0·86	4·72
Samos . .	56	3·98	70·10	22·21	4·00	0·62	2·10

Analyses of the emery of Naxos, Tyre, and Smyrna have been published by R. Jagnaux (Bull. Soc. Min. Fr. 1884, 7, 160). G. Tschermak (Min. Petr. Mitt. 1894, 14, 311) gives analyses and describes the microscopic structure of Naxos emery.

Emery is conveniently employed in the form of 'emery cloth,' 'emery paper,' 'emery sticks,' &c., which are prepared by causing powdered emery to adhere to the glued surface of cloth and other media. 'Emery wheels' are formed by mixing the powdered mineral with some plastic or liquid vehicle, moulding the mass into a convenient shape, and then causing it to set in a solid form. The vehicle may be shellac, or artificial stone, which forms a hard cementing medium, or it may be a paste of loam and water, which is afterwards baked so as to form a coarse terra-cotta. L. J. S.

EMETINE *v.* VEGETO-ALKALOIDS.

EMIN RED *v.* PRIMULINE.

EMODIN *v.* CASCARA SAGRADA; GLUCOSIDES; RHUBARB; SYNTHETIC DRUGS.

EMPYROFORM *v.* SYNTHETIC DRUGS.

EMULSIN. The term 'emulsin' was applied originally to the enzyme or mixture of enzymes, present in bitter and sweet almonds, which hydrolyses amygdalin to glucose, benzaldehyde, and hydrogen cyanide. The same enzyme was shown subsequently to hydrolyse many natural glucosides as well as the synthetically prepared β-glucosides, though it was entirely without action on the stereoisomeric α-alkylglucosides (Fischer, Zeitsch. Physiol. Chem. 1898, 26, 60). The name is now used to comprise all enzymes which hydrolyse β-glucosides. Such enzymes are widely distributed in plants: besides the kernels of fruits, they also occur in the leaves and young twigs of the higher plants, in most mould fungi, especially in *Polyporus* species parasitic on trees, and in bacteria. Henry and Auld (Proc. Roy. Soc. 1905, B, 76, 568) have identified emulsin as present in yeast.

β-Glucosides are also hydrolysed by certain animal extracts, *e.g.* intestinal mucous membrane, a fact which is taken to indicate the presence of emulsin.

There are, however, well-marked differences in the number of substances which these various emulsin preparations are able to hydrolyse, and the investigations of Armstrong and others (Chem. Soc. Proc. 1910, 334) indicate, that whilst the leaf enzyme (emulsin) is, as a rule, a specific for the glucoside normally occurring in the particular plant, the seed enzyme, especially that of the almond, is able to attack a number of glucosides. For this reason almond emulsin is considered to be a mixture of several closely related enzymes. According to H. E. and E. F. Armstrong and Horton (Proc. Roy. Soc. 1908, 80, 321), it contains a *β-glucase* proper, which attacks β-glucosides; a *cyanase*, which eliminates hydrogen cyanide from amygdalin; an *amygdalase*, splitting off glucose from amygdalin; and a *lactase*, acting on milk sugar (compare Rosenthaler, Arch. Pharm. 1910, 240, 105).

Almond emulsin hydrolyses β-glucosides and also the disaccharides, lactose, gentiobiose, cellose, and melibiose. It further hydrolyses the synthetical β-methylgalactoside. The emulsin of *Aspergillus niger*, on the contrary, has no action on lactose or on β-galactosides. In referring to emulsin, it is therefore advisable to specify the source of the enzyme.

Preparation.—Ground sweet almonds from which the fat has been expressed are macerated with water and a little toluene or chloroform at the ordinary temperature for 12–24 hours. The liquid is expressed through a cloth, protein precipitated with a few drops of acetic acid, and the clear filtrate precipitated with alcohol added 50 c.c. at a time till no further precipitate is formed. The liquid is decanted and the precipitate rapidly washed with absolute alcohol and ether to dehydrate it, and dried in a vacuum. Alternatively the original precipitate may be collected on a filter paper, dried roughly on bibulous paper, and dissolved in water in a closed bottle, to which a little toluene is added. The clear solution so obtained is very active, and retains almost constant activity for many months. It is essential to carry out this preparation as rapidly as possible.

The dried enzyme is a soft, white powder, giving most of the reactions of proteins, but losing these on purification. Its chemical nature has not been the subject of any detailed investigation.

Emulsin exhibits maximum activity in neutral solution. Alkali stops the action; small quantities of acids usually increase the activity, owing to their effect in neutralising alkaline impurity.

Experiments with emulsin are usually carried out at about 37°; the optimum temperature is 45°.

Emulsin is detected qualitatively by its action on amygdalin, liberating hydrogen cyanide. The activity is tested quantitatively either against amygdalin or salicin, by measuring the amount of sugar formed in a given time.

Emulsin is also able to bring about synthetic change (Armstrong, Proc. Roy. Soc. 1905, B, 76, 592; van't Hoff, Sitzungsber. K. Akad. Wiss. Berlin, 1910, 48, 963).

(For a list of the glucosides attacked by emulsin, *v.* GLUCOSIDES.) E. F. A.

ENAMEL BLUE. *Cobalt blue* (*v.* PIGMENTS).

ENAMELS are vitreous compositions capable of adhering by fusion to the surface of metal or of pottery. The base of the enamel is generally a colourless glass, in which are suspended particles of an opaque metallic oxide or salt, generally stannic oxide. Up to about 900°, tin dioxide exists finely suspended in the enamel, but at a

higher temperature combination or solution may occur and opacity is diminished. Titanic oxide has been used in place of stannic oxide, and antimony compounds have been employed. Opacity may also be obtained by the use of arsenious oxide, calcium phosphate, cryolite, or fluorspar. A preparation known as 'artificial cryolite' sometimes replaces the mineral. When bone ash is used, a little nitre may be added to remove the grey colour; the nitre also prevents reduction of the lead. The vitreous base of most enamels is a glass containing much lead, but when the presence of lead is objectionable, as in enamelled vessels for culinary purposes, soda- and potash-glasses should be used. If great fusibility be required, it may be secured by the association of borates with the silicates. Borate enamels are very hard, but are deficient in elasticity, and may be affected by moisture. Colour is imparted to the enamels by the introduction of various compounds, generally metallic oxides, the use of which, in many cases, has been known from remote ages. Percy's analyses of the enamelled bricks of Babylonia (*circa* 700 B.C.) showed that a dense white was obtained by the use of stannic oxide; a rich yellow by means of antimony, apparently in the form of lead antimoniate ('Naples yellow'); and a deep blue by copper, probably introduced as oxide, but existing in the enamel as a copper sodium silicate. The ancient Egyptian blue enamel, or glaze, contains a definite copper calcium silicate, forming crystals remarkable for their intense pleochroism, to which Fouqué gave the name of *vestorien* (Bull. Soc. Fr. Min. [12] 1889, 36) (*v.* EGYPTIAN BLUE). The ancient Egyptians seem to have been ignorant of the art of enamelling on metal.

The enamelling of pottery is a simple operation, since it consists in the mere fusion of an opaque glaze on to the surface of the ware. But the application of a vitreous body to a metallic surface is less easy, and it is to this process that the term 'enamelling' is sometimes restricted, while the works of art produced by enamelling on metal are themselves known as 'enamels.'

The most ancient enamels found in North-Western Europe are referable to the prehistoric Iron Age, sometimes distinguished as Late Celtic. In these ancient enamels, brilliantly coloured opaque glass is embedded in cells or shallow cavities in bronze: it is probable that the vitreous material was applied as a powder, mixed with a vehicle so as to form a paste, and then heated sufficiently to cause its fusion, and thus secure firm attachment to the metal.

A similar method, known as *champ levé* enamelling, was extensively employed at a much later date in Germany and at Limoges in France —a town which for centuries was the chief centre of artistic enamelling. In this process the design is traced on a plate of copper or bronze, and all the parts to be enamelled are excavated by the graver; these hollows are then filled with enamel, which is afterwards fused, and the entire surface is finally ground smooth. The design thus appears in permanent colour, each tint being defined by ridges, or separated by areas, of metal which are the elevated parts of the original ground. The exposed metal is sometimes gilt.

Another and probably older method of inlaid enamelling is that known as *cloisonné* work. Here the design is outlined by strips of metal fixed to the metallic base, and the spaces between these bands are filled with enamel, which is then fused and the surface ground down. Each coloured area is, therefore, sharply separated from its neighbour by the edge of the metal fillet. Of this character were the early Byzantine enamels, which were generally executed on plates of gold. The Chinese have for many centuries (at least since the 13th) been extremely skilful in this work, and the Japanese have applied a similar method to the ornamentation of porcelain. The Japanese attach the cloisons to the base with a gummy cement, and even when the ground is a metal, they generally use no solder. In some *cloisonné* work the surface is not ground down, so that the fillets stand in relief above the general surface of the enamel.

The use of transparent enamels for the ornamentation of metalwork was introduced by the Italian goldsmiths of the 13th century, and afterwards became popular in France. The design was generally worked in low relief, or chased on gold or silver, and brilliant translucent enamels were applied in such a way that the varying thicknesses produced differences of tint. This style is known as *basse-taille*. In certain rare enamels, probably of the 15th century, the pattern is outlined by strips of metal without any foundation, and the spaces in this grating are filled in with coloured transparent enamels; such *cloisonné* work is termed *plique-à-jour*.

Artistic enamelling has been largely used, not only for inlaid and encrusted work, but for the production of paintings on metal. The painted enamels of Limoges, introduced in the 15th century, were usually executed on slightly convex plates of copper, the subjects being generally in white and grey on a deep-violet ground; but the process was extended to the decoration of dishes, ewers, and other objects, and various colours were employed, sometimes heightened with gold. In this country, enamel painting was largely practised, by the family of Bone, during the latter part of the 18th and the early years of the following century. While their smaller works, or miniatures, were executed on gold, the larger examples were on plates of copper. The copper plate, having been annealed and cleaned with dilute sulphuric acid, was coated on both sides with white enamel powder; it was then fired, and the enamelled face ground smooth. This white enamel, which was rendered so opaque by means of stannic oxide as to conceal the metal ground, was imported from Venice in the form of round cakes. The surface to be painted was further prepared by the application of a second coat of enamel, more fusible and transparent than the first; this material, known to the enameller as 'flux,' was used in the form of rods and beads of white Venetian glass. Upon the fluxed surface, carefully ground smooth, the painting was executed in enamel colours, or powdered glasses mixed with an appropriate vehicle; and as it was necessary to vitrify each colour separately, a complicated subject would require several successive firings in a muffle, each liable to injure or spoil the work.

Recent years have witnessed a great revival in artistic enamelling, with the introduction of various improvements in technical details.

In addition to art enamels, there is a growing demand for coarse work in enamelled sheet-iron for street plates, railway notices, and other advertisements, which are generally executed in blue and white. In applying enamel to metal it is necessary to use a material which will adhere firmly to the base; at the same time, it must fuse at a temperature lower than that which softens the metal, or melts the solder if any be present; and the enamel should have a coefficient of expansion by heat as nearly as possible that of the metal ground. It is obviously important that, when enamel is used as a lining for saucepans, stew-pans, and other vessels for culinary purposes, it should be free from all ingredients which are poisonous, or may become so by contact with food. An important industry has been developed in recent years, especially in Germany, Austria-Hungary, and France, in the manufacture of vessels for domestic use, in cast or sheet metal; soft sheet steel is commonly used for hollow ware.

The object to be enamelled, having been carefully cleaned by pickling in an acid bath, is coated with a thin layer of ground enamel. This primary coating need not be opaque, and generally contains a little cobalt or nickel oxide. A suitable material is obtained, according to P. Randau, by fusing a mixture of flint or quartz 30 parts, borax 25, and felspar 30. This product is then ground with kaolin 10·75 parts, felspar 6, and magnesia 1·25; the clay tends to lessen the fusibility. The finely powdered ground enamel is mixed with water to a creamy consistency and applied to the ware, slightly heated; after the coating has dried, the object is fired in a muffle furnace at a temperature rather under 1000°. After this stage of enamelling, the ware is scrubbed to remove scale, and a second coating is applied, this time opaque white. This enamel may be made, according to the same authority, from a mixture of flint 37·5 parts, borax 27·5, tin dioxide 30, soda 15, nitre 10, ammonium carbonate 7·5, and magnesia 7; this mixture is fritted and then ground with flint 6·12 parts, tin dioxide 3·66, soda 0·7, and magnesia 0·7. The cover enamel is suspended in water and spread over the ground enamel, and the ware is then carefully fired in a muffle at a lower temperature than that of the first firing. In some cases a third coat of enamel is applied, while in other cases the ground layer is dispensed with, and only a single white coating used. Finally the surface may be decorated by painting or transfer printing in enamel colours, or by photographs. In some enamels, like 'granite ware,' the colour is applied by spraying.

(On enamels, *v.* Sir H. H. Cunynghame, On the Theory and Practice of Art Enamelling upon Metals, 3rd ed. London, 1906; Lewis F. Day, Enamelling, London, 1907; Alexander Fisher, The Art of Enamelling upon Metal, London, 1906; Philipp Eyer, Die Eisenemaillierung, Leipzig, 1907; Paul Randau, Die Fabrikation des Emails und das Emaillieren, Vienna, 4th ed. 1909; Enamels and Enamelling, English translation of P. Randau by Charles Salter, London, 1900; Julius Grünwald, translated by Herbert H. Hodgson, The Theory and Practice of Enamelling on Iron and Steel, London, 1909). F. W. R.

ENARGITE. Copper sulpharsenate Cu_3AsS_4 or $3Cu_2S{\cdot}As_2S_5$, occurring as orthorhombic crystals with perfect prismatic cleavages and usually a prismatic habit. The colour is iron-black with a metallic lustre; sp.gr. 4·44. It is not a common mineral, but in a few copper-mining districts, particularly at Butte in Montana, it is an important ore of copper. L. J. S.

ENDIVE. *Cichorium endivia* (Linn.), the blanched leaves are used as a salad or garnish.

According to König, their average composition is—

Water	Protein	Fat	Sugar	Other carbohydrates	Fibre	Ash
94·1	1·8	0·1	0·8	1·8	0·6	0·8

There are two chief varieties—with crinkled leaves and with smooth leaves. The former is apparently richer in nitrogen and ash, but poorer in carbohydrates (Dahlen, Landw. Jahrb. 1874, 3, 312, and 4, 614).

An analysis of the ash of endives by Richardson (Annalen, 67, 377) gave the following figures:—

K_2O	Na_2O	CaO	MgO	SO_3	P_2O_5	SiO_2	Fe_2O_3
37·9	12·1	12·0	1·8	5·2	3·0	24·6	3·4

H. I.

ENDLICHITE *v.* VANADIUM.

ENESOL *v.* SYNTHETIC DRUGS.

ENGLISH BROWN *v.* AZO- COLOURING MATTERS.

ENGLISH GREEN, or **CHROME GREEN,** *v.* CHROMIUM; PIGMENTS.

ENGLISH PINK, or **ITALIAN PINK,** *v.* PIGMENTS.

ENGLISH RED, or **VENETIAN RED,** *v.* PIGMENTS.

ENHYDROS *v.* AGATE.

ENSILAGE is a process of preserving green fodder for cattle. The term *silo* is applied to the pit or other depository in which the fodder (*silage*) is contained, and appears to be of Basque derivation, and originally meant a pit for storing grain. This method of preserving grass and other succulent forage crops has been in use for many years in Germany, whence the practice was carried to France, and afterwards to America. Although the German system had been fully described by Johnston, in 1843, in the Transaction of the Highland Agricultural Society (new series, 9), no general notice of it was taken in these islands until 1882, when a report of the British Legation at Washington on ensilage, as practised on Mr. Havemeyer's estate in New Jersey, was published as a blue-book, since which time many silos, of varying forms and construction, have been made in this country. The object of all these is to exclude the air from the mass of fodder, allowing only a greater or less fermentation according to the practice of different authorities; and to this end silos have been formed (1) wholly or partly underground; (2) in the form of enclosed buildings. Silage has also been largely made by building up the green fodder in the form of an ordinary stack, of which only the top is covered. Whether it be silo or stack, the principal factor is the superposition of a sufficient pressure, either by dead weight or by some mechanical system of screws, levers, or similar appliances. The changes which forage undergoes in the silo

are due to fermentation, and, as may be supposed, this action varies considerably with the materials stored and with the condition of storage; as, for example, green maize undergoes principally lactic fermentation; whilst in English fodder fermentation produces alcohol, which is almost immediately converted into aldehyde. If the air has not been properly expelled from the silo, or if the fodder has been pitted in a very damp condition, the aldehyde becomes quickly converted into acetic acid.

Silage is of two kinds—viz. 'sweet' and 'sour.' Sweet silage is the result of allowing the grass to remain without pressure, and so permitting air to mingle with it until such time as a temperature of 125° to 150°F. is reached by the fermentation process; sour silage, on the other hand, results when pressure is at once applied, whereupon an acetic or lactic fermentation takes place. It appears that a temperature of about 125° is sufficient to kill the bacteria which produce acid fermentation; 'if the bacteria are killed and the silo is covered and weighted, the enclosed mass of green fodder will remain sweet, and be practically preserved under the same conditions as fruits, vegetables, or meats are preserved when canned. If this be the case, it will be at once intelligible that by less packing of the fodder when put into the silo, and extending the time of filling until the temperature rises to a point fatal to the bacteria, the resulting silage will be sweet and free from acidity; whilst sour silage is produced by at once consolidating, covering up, and weighting the grass fodder so as to prevent the temperature rising to the point fatal to the bacteria' (A. Voelcker, J. Roy. Agric. Soc. 20).

Two samples of sweet silage showed only a trace of acid, not exceeding in quantity that contained in ordinary fresh meadow grass:—

—	Silage made from	
	Clover and rye grass mixed	Meadow grass
Moisture	75·80	74·40
*Albuminoids	2·53	2·56
Sugar and other carbohydrates soluble in water	1·43	2·99
Crude vegetable fibre	18·31	17·00
Mineral matter (ash)	1·93	2·15
	100·00	100·00
*Containing nitrogen	0·40	0·41
Volatile acids (calculated as acetic acid)	0·01	0·04
Non-volatile acids (calculated as lactic acid)	0·01	0·02

A sample of sour silage made from grass placed in a heavily weighted silo showed the following composition:—

Water	76·01
Soluble albuminoids	0·91
Insoluble albuminoids	1·78
Soluble carbohydrates	2·87
Crude fibre	15·82
Soluble mineral (ash)	1·63
Insoluble mineral matter (ash)	0·98
	100·00
Total nitrogen	0·43
Volatile acids (calculated as acetic acid)	0·19
Non-volatile acids (calculated as lactic acid)	1·24

This silo was provided with a tap at the bottom from which juice was drawn off from time to time. This drainage had a sp.gr. of 1·022, and contained, per imperial gallon:

	Grains
Albuminoids	1,008·56
Fixed acid (lactic acid)	516·42
Volatile acids (butyric and acetic acids)	476·79
*Carbohydrates and amides	1,528·42
Mineral matters (ash)	1,768·20
Water	64,701·70
	70,000·00
*Containing non-albuminous nitrogen	35·84

The dry matter (dried at 100°) which was left on evaporation of its drainage contained:

*Albuminoids	20·90
Lactic acid	10·71
†Carbohydrates and amides	31·73
Mineral matter (ash)	36·66
	100·00
*Containing nitrogen	3·34
†Containing nitrogen	0·51

The subject of changes during ensilage have been very carefully investigated both at Rothamsted by Lawes and Gilbert, and at Woburn by Voelcker. The results obtained present a striking similarity, and it will suffice if one set of tables (those of Dr. Voelcker) is referred to here, although the Experiments on Ensilage conducted at Rothamsted (Lawes and Gilbert) should also be read. The silo to which these figures relate was one made at Woburn in 1886, and was of the character generally termed 'sour.' It was weighted with stones in strong elm boxes to 112 lbs. per square foot, and was unprovided with any drain. The silo was closed on July 3 and opened on December 16, the contents being 'very fair,' although 'not really fine,' meadow grass. The numbers, in a condensed form, are given in the table, p. 337.

The main features shown in the table are as follows: The total loss due to fermentation, evaporation, &c., in making the silage was 7·29 p.c. on the fresh grass. Of this, 3¼ p.c. consisted of water, so that the loss in dry matter was only about 4 p.c. The loss of total nitrogen when, as here, no drainage was allowed to flow away, is very slight; but the nitrogenous bodies have undergone considerable change from the albuminoid to the non-albuminoid condition, the fibre has been diminished, insoluble albuminoids have been lessened, and soluble albuminoids increased (Voelcker, J. Roy. Agric. Soc. 23, 410).

Since the nutritive value of food depends to a considerable extent on the albuminoid compounds contained in it, it becomes of importance from the economic point of view, to determine the quantity of such compounds in fresh green food and in silage. Kinch found that 55 p.c. of the total nitrogen present in the silage of grass was of a non-albuminoid nature, whilst in the original grass only 9 p.c. was of this

QUALITY AND COMPOSITION OF THE GRASS PUT INTO SILO, AND OF THE SILAGE PRODUCED.

	Total weight	Water	Volatile acids	Non-volatile acids	Soluble albuminoids	Insoluble albuminoids	Digestible fibre	Woody fibre	Soluble carbohydrates, &c.	Soluble mineral matter	Insoluble mineral matter	Total nitrogen	Albuminoid nitrogen	Non-albuminoid nitrogen
	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.
Grass put in silo	32,780	23,108	—	—	47	733	3278	2670	2265	430	249	151	123	28
Silage removed .	30,389	22,035	109	106	197	252	2326	2409	2254	471	230	155	73	82
Loss . . .	2,391	1,073	+109	+106	+150	481	952	261	11	+41	19	+4	50	+54
Loss per 100 lbs. of fresh grass .	7·29	3·27	+0·33	+0·32	+0·46	1·47	2·90	0·79	0·03	+0·12	0·06	+0·01	0·15	+0·16

form. In the case of mangold leaves, Kellner found that of the total nitrogen present, 27·8 p.c. in the original leaves, 45·5 p.c. in the silage, and as much as 59·7 p.c. in silage preserved in stoppered jars, was non-albuminoid. Clifford Richardson, examining maize silage, found:

	Per cent. total nitrogen as non-albuminoid
Original stalks . . .	21·2
Silage, No. 1 . . .	44·6
„ No. 2 . . .	49 6
Dried fodder . . .	15·6
Silage from young maize .	53·3
„ „ older „ .	47·1

These results with grass, mangolds, and maize show that in ensilage a large portion of the albuminoids are converted into non-albuminoid nitrogenous substances, whilst in the ordinary drying of fodder no such change seems to take place. This is made clear by a reference to Dr. Voelcker's table given above under the heading 'Quality and composition,' &c., where the woody fibre, as indeed the whole of the fibre, has been diminished, insoluble albuminoids are lessened, and the soluble albuminoids increased.

Ensilage is largely practised in Canada and in America for the sake of having a supply of 'green' fodder during the winter months, especially in Canada where the winter is long. In England, since the interest attaching to novelty has waned, it has gradually died out of practice, except as a resource for adoption in unusually wet seasons, when haymaking is impossible or is so long delayed as to threaten loss of the crops. In such circumstances those who possess the simple tackle necessary for putting up silage stacks in the open field have a material advantage over their neighbours. Otherwise, in a country in which roots are easily grown and preserved for winter use, and where the actual period of the year in which vegetation is suspended is comparatively short, it would seem preferable, having regard to the deterioration which occurs in ensilage, especially as regards albuminoids, to adhere to the more ordinary practice of hay-making.

The application of silage as fodder and its practical effects with stock have been carefully investigated both at Rothamsted and Woburn.

(*See* Report on the Practice of Ensilage at Home and Abroad, Jenkins in J. Roy. Agric. Soc., new series, 20; On the Chemistry of Ensilage, Voelcker, *ibid.*; Experiments on Ensilage conducted at Crawley Mill Farm, Woburn, 1884–5 and 1885–6, Voelcker, *ibid.* 22; Experiments on Ensilage conducted at Crawley Mill Farm, Woburn 1886–7, Voelcker, *ibid.* 23; articles in the Agricultural Gazette, April 27, 1885 *et seq.*, by Sir J. B. Lawes and Sir Henry Gilbert, reprinted in pamphlet form under the title of Experiments on Ensilage conducted at Rothamsted.)

ENTEROL *v.* SYNTHETIC DRUGS.

ENZYMES and **ENZYME ACTION** *v.* FERMENTATION; BARLEY; CHEMICAL AFFINITY.

EOSAMINE *v.* AZO- COLOURING MATTERS.

EOSIN *v.* TRIPHENYL METHANE COLOURING MATTERS.

EOSOTE *v.* SYNTHETIC DRUGS.

EPHEDRINE. Spehr (Chem. Soc. Abstr. 1892, 893) obtained an alkaloid which he called ephedrine from *Ephedra monostachya*, of very feeble physiological action, of the formula $C_{13}H_{18}NO$; m.p. 112°; volatilising at about 125°.

Nagai (Chem. Zeit. 1890, 441) isolated an alkaloid from the stems of *Ephedra vulgaris*, to which he also gave the name ephedrine; it was a powerful mydriatic, had the empirical formula $C_{10}H_{15}NO$, and yielded benzoic acid, monomethylamine, and oxalic acid on oxidation.

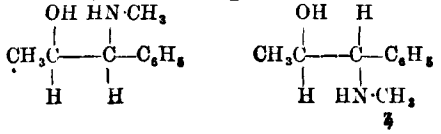
iso*Ephedrine* he describes as obtained on heating normal ephedrine at 180° in sealed tubes with hydrochloric acid.

A similar alkaloid, with strong toxic and mydriatic properties, was isolated from other plants of the same genus by Merck, and provisionally termed *ψ-ephedrine*. Its physical and chemical characteristics were examined by Ladenburg, and Oelschlägel (Ber. 22, 1823); Miller (Arch. Pharm. 1902, 240, 481) could only obtain ψ-ephedrine from *Ephedra vulgaris*, and Flaecher (Arch. Pharm. 1904, 242, 380) has shown that Nagai's *iso*ephedrine and the ψ-ephedrine of Ladenburg and Oelschlägel are identical.

Either base heated with hydrochloric acid gives an equilibrium mixture of both (Schmidt, *ibid.* 1908, 246, 210).

Ephedrine is completely converted into ψ-ephedrine on acetylation, the same acetyl derivative $C_{10}H_{14}ON(C_2H_3O),HCl$, m.p. 175°, $[\alpha]_D$ +97·6°, being formed from both bases, and yielding ψ-ephedrine on hydrolysis (Apoth. Zeit. 1910, 25, 677–678); while the alcohol produced from ψ-ephedrine by Hofmann's degradation is converted by repeated distillation into that from ephedrine (Emde, Arch. Pharm. 1907, 245, 662).

Ephedrine and ψ-ephedrine are optical isomerides, with the configurations shown below:



the reversible conversion with hydrochloric acid being due to racemisation of the right-hand portion of the molecule (Emde, Arch. Pharm. *l.c.*; Gadamer, *ibid.* 1908, 246, 566).

Fourneau (J. Pharm. Chim. 1904, 20, 481) describes the synthesis of four isomerides of ephedrine with varying physiological action. The crystallographic constants are given by Schwantke (Zeitsch. Kryst. Min. 1909, 46, 73).

Ephedrine hydrochloride (*ephedrinum hydrochloricum*) is readily soluble in water, and has a strong mydriatic action, 1–2 drops of a 10 p.c. solution producing in 40–60 minutes a marked dilation lasting 5–20 hours. It has been used in place of atropine and homatropine.

EPICARIN *v.* SYNTHETIC DRUGS.

EPICHLORHYDRINS *α-epichlorhydrin* (*γ-chlorpropylene oxide*) $CH_2\langle O \rangle CH\cdot CH_2Cl$. Prepared by treating glycerol with phosphorus pentachloride or by heating the dichlorhydrins with hydrochloric acid (Berthelot, Ann. Chim. Phys. [3] 41, 299); by treating α- or β-dichlorhydrin with caustic potash (Reboul, Annalen, Spl. 1, 221; Tollens and Münder, Zeitsch. Chem. 1871, 252). Glycerol is treated with hydrogen chloride at 120°–130°, and the product distilled *in vacuô*. The fraction boiling at 50°–120°, which contains the dichlorhydrins, is treated with strong caustic potash solution, and the product distilled *in vacuô*. The portion boiling below 75° is washed with water and distilled. The fraction boiling at 116°–118° is crude epichlorhydrin, and may be purified by redistillation *in vacuô* (Fauconnier, Bull. Soc. chim. ii. 50, 212). Mobile liquid with odour resembling that of chloroform; b.p. 116·6° (corr.); sp.gr. 1·2031 at 0°/4° (Thorpe, Chem. Soc. Trans. 1880, 206); insoluble in water. With sodium in ethereal solution epichlorhydrin yields allyl alcohol and the diallyl ether of glycerol (Tornoï, Ber. 1888, 1290; Kijner, J. Russ. Phys. Chem. Soc. 24, 31); by heating with alkyl iodides, chloriodohydrin alkyl ethers are produced (Paal, Ber. 1888, 2971); ammonia gas converts it into trichlorhydroxypropylamine (Fauconnier, Compt. rend. 107, 115); with potash in the presence of an alcohol, it yields the corresponding dialkyl ether of glycerol (Zunino, Atti. Real. Accad. Lincei, 1897, ii. 348; 1907, 9, i. 309); with phenols and sodium ethoxide, glyceryl diaryl ethers are formed; whilst with sodium hydroxide, glycide aryl ethers are produced (Boyd and Marle, Chem. Soc. Trans. 1908, 838; 1909, 1803; Zunino, Atti. Real. Accad. Lincei, 18, i. 254; Cohn and Plohn, Ber. 1907, 2597; Lindemann, *ibid.* 1891, 2145); concentrated nitric acid oxidises it to β-chlorlactic acid; alcoholic ammonia and ethylsodiomalonate convert it into chlorhydroxypropylmalonamide (Traube and Lehmann, Ber. 1899, 720). Haller and March have synthesised ketolactonic acids and other unsaturated compounds by condensing epichlorhydrin with the sodium derivatives of benzoyl acetic esters, of acetone dicarboxylic ester and of acetylacetone (Compt. rend. 132, 1459; 136, 434; 137, 11, 1203). It has also been condensed with aniline (Fauconnier, *ibid.* 106, 605; 107, 250); with *p*-toluidine (Cohn and Friedländer, Ber. 1904, 3037); with prussic acid (Lespieau, Compt. rend. 127, 965), and with salicylic acid (Lange, D. R. P. 184382; Chem. Soc. Abstr. 1906, i. 930). Organomagnesium compounds react with it to form substituted chlorhydrins of the type $R\cdot CH\langle CH_2OH / CH_2Cl$ (Riedel, Chem. Zentr. 1907, i. 1607; D. R. P. 183361; Fourneau and Tiffeneau, Bull. Soc. chim. 1, [4] 1227). Epichlorhydrin has been used as a solvent for resins for photographic purposes (Phot. Korr. 1899, 2).

β - Epichlorhydrin (*β - chlorpropylene oxide*) $CH_2\langle O \rangle CHCl\cdot CH_2$. Obtained together with the α- compound and other products by treating the chloriodohydrins formed by treating allyl alcohol with iodine monochloride, with dry sodium hydroxide (Bigot, Ann. Chim. Phys. 22 [6] 468). Liquid; b.p. 132°–134°. Phosphorus pentachloride converts it into βγ-dichloropropylene, and sodium amalgam into allyl alcohol.

Polymerides. $(C_3H_5OCl)_2$. Obtained in the preparation of pyrazine bases by the distillation of glycerol with ammonium phosphate and ammonium chloride; by treating the high-boiling fractions with hydrochloric acid, it is obtained crystalline; m.p. 112°–113°; b.p. 232°–233°. Readily soluble in hot alcohol, sparingly soluble in water.

$(C_3H_5OCl)_6$. Obtained by treating α-epichlorhydrin with hydrofluoric acid in a platinum dish. Yellow oil, soluble in alcohol, benzene, ether, or acetic acid. Dilute sulphuric acid at 200° converts it into a substance resembling cellulose (Paternò and Olivieri, Gazz. chim. ital. 24, i. 305; ii. 541).

Chlorbutylene oxide C_4H_7OCl. Obtained by treating a mixture of butenylglycerol and glacial acetic acid with hydrogen chloride; b.p. 125·5° (corr.) at 738 mm.; sp.gr. 1·098 at 15°/0 (Zikes, Monatsh. 6, 352).

EPINEPHRINE *v.* ADRENALINE; also SYNTHETIC DRUGS.

EPIRENAN *v.* SYNTHETIC DRUGS.

EPSOM SALTS. *Magnesium sulphate* (*v.* MAGNESIUM).

EQUILIBRIUM *v.* CHEMICAL AFFINITY.

ERBIUM. Sym. Er. At. wt. 167·7. A dark-grey powder; sp.gr. 4·77 at 15° (S. Meyer, Monatsh. 1899, 20, 793).

Sources.—Ytterbite (gadolinite), yttrotantalite, euxenite, xenotime.

The oxide of this metal belongs to the group of yttrium earths, forming with dysprosium and thulium the erbium sub-group, the salts of which are distinguished by their colour and by their characteristic absorption spectra in solution.

Separation and purification of the yttrium earths. The following methods have been employed in separating the closely related members of the yttrium earths:

1. *Fractional decomposition of nitrates* (Bahr and Bunsen, Annalen, 1866, 137, 1). The nitrates, heated until nitrous fumes are evolved, leave a vitreous residue of basic nitrates, the solutions of which, in hot water, slowly deposit, on cooling, small pink needles containing the greater proportion of the coloured erbium earths. The crystals are extracted with 3 p.c. nitric acid, the solution evaporated, the residue again heated, and the whole series of operations repeated many times. The erbium earths

accumulate in the less soluble basic salts, whilst the remaining yttrium earths, and any cerium earths which may be present, accumulate in the final mother liquors, and are not readily freed completely from the erbium earths. Further separation is effected by heating these nitrates from the final mother liquors so strongly that the residue consists of oxides mixed with insoluble basic nitrates. On extraction with water, the erbium compounds remain undissolved, and the operation is repeated till the more soluble yttrium salts no longer show absorption bands.

2. *Differences in the solubility of the oxides.*—The oxides are mixed with water and treated with an amount of nitric acid insufficient to convert the oxides into normal nitrates. The mixture becomes hot, and after cooling, concentrated nitric acid is added until the product assumes a reddish tint. The precipitate is then digested with alcohol, which dissolves the normal nitrate, to the exclusion of the basic nitrates. The latter consist chiefly of erbium salts mixed with some ytterbium and scandium compounds, the more basic yttrium and cerite metals passing into solution. The final separation of erbium from ytterbium and scandium is effected by fractionally precipitating the basic nitrates by adding oxides to the solution of normal nitrates. In this operation ytterbium and scandium are precipitated as basic nitrates, while erbium remains dissolved (*v.* Drossbach, Ber. 1902, 35, 2826).

3. *Fractional precipitation by alkalis or aniline.*—The addition of ammonia to hot solutions of the salts of the yttrium group occasions the precipitation of basic salts which are easily filtered.

The neutral chloride dissolved in 50 p.c. alcohol is decomposed at 90° with alcoholic aniline, or the hydroxide is treated with aniline hydrochloride in aqueous solution (Drossbach, Ber. 1896, 29, 2452; Mullmann and Baur, *ibid.* 1900, 33, 1748; 1902, 35, 2382; Urbain, Compt. rend. 1901, 132, 136; Krüss, Annalen, 1891, 265, 1; Zeitsch. anorg. Chem. 1893, 3, 108, 353, 407).

4. *Fractionation with ammonium carbonate and acetic acid.*—The hydroxides of the yttrium group are moderately soluble in concentrated aqueous ammonium carbonate, and from this solution the earths may be fractionally precipitated by acetic acid (Dennis and Dales, J. Amer. Chem. Soc. 1902, 24, 400).

5. *Fractionation of oxalates, acetates, acetylacetonates, ethylsulphates* (Urbain, Ann. Chim. Phys. 1900, [7] 19, 184; Marc, Ber. 1902, 35, 2370); *formates* (K. A. Hofmann, *ibid.* 1908, 41, 308); *ferrocyanides* (Böhm, Die Darstellung der seltenen Erden); *bromates* (James, J. Amer. Chem. Soc. 1908, 30, 182); *chromates* (Krüss and Zoose, Zeitsch. anorg. Chem. 1893, 3, 92).

Erbia (*erbium oxide*) Er_2O_3. A pink powder obtained by heating the oxalate at 575°–845°; sp.gr. 8·64; sp.ht. 0·065.

The salts of erbium have a pink or reddish colour, a sweet, astringent taste, and their solutions exhibit characteristic absorption bands in the red, green, and blue regions of the spectrum. The wave lengths corresponding with the two most prominent bands are as follows: λ·522·5–523·5 and 647·5–651·5.

Unless ionic dissociation is repressed, dilute solutions of the various erbium salts exhibit identical absorption spectra (Zeitsch. physikal. Chem. 1906, 56, 624; *v.* Purvis, Proc. Camb. Phil. Soc. 1903, 12, 202, 206). The absorption bands undergo displacement when the solutions are placed in a magnetic field (J. Becquerel, Compt. rend. 1907, 145, 1412).

(For accounts of the flame, spark, and arc emission spectra, *v.* Thalén, *ibid.* 1880, 91, 326; Exner and Haschek, Wien. Akad. Ber. 1899, 108, IIa, 1071, 1123.)

Erbium salts exhibit signs of radio-activity (Strong, Amer. Chem. J. 1909, 42, 147).

Erbium sulphate $Er_2(SO_4)_3,8H_2O$. Pink monoclinic crystals, separating from aqueous solution at 20°–25°; isomorphous with the corresponding yttrium, praseodymium, and neodymium salts (Kraus, Zeitsch. Cryst. 1901, 34, 307).

The double sulphates $Er_2(SO_4)_3,K_2SO_4,4H_2O$ and $Er_2(SO_4)_3,(NH_4)_2SO_4,4H_2O$, are readily soluble in cold water.

Erbium nitrate $Er(NO_3)_3,5H_2O$. Large reddish crystals stable in air. When heated on platinum wire, the nitrate imparts an intense greenish colour to the flame, which, when viewed through the spectroscope, shows bright lines in the yellow-green and orange-blue regions of the spectrum. These bright lines correspond in position with the dark bands of the absorption spectrum.

Erbium formate $Er(CHO_2)_3,2H_2O$. Crystallises from cold aqueous solution.

Erbium oxalate $Er_2(C_2O_4)_3,10H_2O$ (K. A. Hofmann, Ber. 1910, 43, 2631) is a reddish, sparingly soluble microcrystalline powder.

Erbium platinocyanide $Er_2[Pt(CN)_4]_3,21H_2O$, like the corresponding yttrium salt, crystallises in red prisms with a green metallic reflex.

G. T. M.

ERECTHIDIS OIL consists of a terpene $C_{10}H_{16}$, which boils at 175°, and at 18·5° has a sp.gr. of 0·838. This body absorbs a molecule of hydrochloric acid without the separation of a crystalline compound. The portion of the oil which boils above 200° also consists of a terpene (Beilstein and Wiegand, Ber. 15, 2854).

EREPSIN *v. Enzymes*, art. FERMENTATION.

ERGOT OF RYE. *Spurred rye*; *Ergota*; *Secale cornutum.* (*Ergot de seigle*, Fr.; *Mutterkorn*, Ger.) Ergot of rye consists of the compact mycelium or spawn, the nutritive organ, of the fungus *Claviceps purpurea* (Tulasne), developed within the paleæ of the rye fruits. The same fungus grows upon the fruits of other members of the natural order *Gramineæ*, giving rise to less-known ergots, as, for instance, *ergot of wheat* or *ergot of oat.* The fungus is collected in the second or intermediate stage of its development, in which it remains dormant for many months. At this period it is noticeable projecting out of the heads of the rye as long, narrow, slightly arched grains of a purplish black colour and horny consistence. Ergot has been known for some three hundred years, and is an agent of great importance in medicine. Its chief action is that of a stimulant of the uterine muscles. It is employed in cases of insufficient contractile power, and as a remedy for uterine and other forms of hæmorrhage. (Further botanical and historical

particulars are given by Flückiger and Hanbury (Flück. a. Hanb. 740); Pereira, Mat. Med. 3rd ed. 2, 996; Cooke, Brit. Fungi, 772; Pharm. J. [3] 1, 702; Bentl. a. Trim. 303; Stoddart, Pharm. J. [3] 10, 194; Wilson, *ibid.* [3] 6, 525, 545, and 564; Parsons, Rep. U.S. Commissioner Agriculture, 1880, 136; Holmes, Pharm. J. [3] 16, 684.)

Ergot when kept undergoes decomposition of a kind which affects materially its physiological activity. To prevent this, many methods of preservation have been suggested. These depend generally either upon removal of the oil by a solvent such as light petroleum, or by expression, or on the addition of some substance such as ether or benzoïn which surrounds the drug with an antiseptic vapour (*v.* Gobley, J. Pharm. Chim. [4] 17, 217; Ducros, Z. oesterr. Apoth. V. 1876, 8; Gionvié, *ibid.* 1876, 126; Perret, Bull. Gen. Thérap. 1882, 202; Moss, Pharm. J. [3] 16, 274).

Few articles of materia medica have been more studied chemically than ergot, but of the numerous more or less definite constituents which have been isolated, there were none that represented in a satisfactory manner the physiological activity of the drug, or at all events that were available to the therapeutist. Thus ergot is still administered in the form of aqueous or other extract more or less concentrated and freed from inactive constituents. Formulæ for these pharmaceutical preparations, which are liable generally to the same deteriorations on keeping as the drug itself, find their place in the various pharmacopœias. One of the most celebrated extracts of ergot, *ergotin* or *ergotine*, is that of the French pharmacist Bonjean (J. Pharm. Chim. 1843, 4, 107; Compt. rend. July 17, 1843). (For examples of others, *v.* Long, Med. Press Cir. 8, 435; Ronayne, *ibid.* 9, 267; Squibb, Proc. Amer. Pharm. Assoc. 1873, 957; Gerrard, Pharm. J. [3] 5, 805; 13, 235; Wernich, Y.-Book Ph. 1875, 349; Carles, J. Pharm. Chim. 1878, 28, 45; Active Principle of Ergot of Rye, Pharm. J. [3] 6, 942; 7, 4; Zellhoefer, Proc. Amer. Pharm. Assoc. 1877, 404; Yvon, Révue Méd. Nov. 15, 1879; Catillon, Y.-Book Ph. 1880, 305; Diehl, Pharm. J. [3] 12, 519; Hallberg, Amer. J. Pharm. 1883, 8; Conrad, Y.-Book Ph. 1883, 299; Denzel and Wacker, Arch. Pharm. [3] 22, 314; Clark, Pharm. J. [3] 16, 521; Engelmann, Y.-Book Ph. 1887, 276).

Vauquelin, in 1816, made a chemical analysis of ergot (Ann. Chim. Phys. 3, 337), and among other early investigators are Pettenkofer, Rep. Pharm. 3, 65; Winkler (Christison on Poisons); Ludwig, Arch. Pharm. [2] 114, 193; Wiggers, Annalen, 1, 129; J. Pharm. Chim. 18, 525; Chevallier, Neuest. Entd. Mat. Med. 1837, 129. The results obtained by Wiggers, which were confirmed in their main points by Chevallier, may be taken to represent those researches. That observer finds 35 p.c. of *fixed oil*, after removal of which with ether an alcoholic extract of the residue is prepared, and this on evaporation and washing of the residue with water, leaves 1½ p.c. of a very active resinous substance to which the name *ergotine* was applied.

About the year 1865 Wenzell (Vierteljahresschrift prakt. Pharm. 14, 18) announced the discovery of three new compounds obtained from ergot: two amorphous alkaloids, *ergotine* and *ecboline*, and a volatile acid with which they are combined, *ergotic acid*. This ergotine must not be confused either with pharmaceutical preparations such as Bonjean's ergotine or with indefinite substances like Wigger's ergotine. The research of Wenzell was confirmed and extended by Manassewitz (Pharm. Zeit. 6, 387), Hermann (Vierteljahresschrift prakt. Pharm. 18, 481; Neues Rep. Pharm. 20, 283), and Ganser (Arch. Pharm. 144, 193; Neues Rep. Pharm. 20, 301).

Tanret, in 1875 (Compt. rend. 81, 896; 86, 888; Ann. Chim. Phys. [5] 17, 493; J. Pharm. Chim. 26, 320), announced the discovery of an active crystalline alkaloid which he named *ergotinine* in order to distinguish it from the resinous ergotin of previous investigators. From the mother liquors of this base, Tanret obtained a further yield of alkaloid in an amorphous form. This was called *amorphous ergotinine*, since, in other respects, it closely resembled the crystalline product.

A further examination of ergot was conducted by Dragendorff and his pupils (Dragendorff and Podwissotzky, Pharm. J. [3] 6, 1001; Neuer. Jahresb. Pharm. 1877, 39; Podwissotzky, Y.-Book Ph. 1884, 87; Blumberg, Pharm. J. [3] 9, 23, 66, 147 and 598). Several substances were obtained and analysed, but their state of purity was not sufficient to characterise them as individual compounds.

Kobert (Chem. Zentr. 1885, 66) also announced the discovery of three new compounds in ergot, *cornutine*, *ergotic*, and *sphacelinic acids*. Tanret (J. Pharm. Chim. 11, 309), however, questioned the existence of these compounds, and came to the conclusion that cornutine is ergotinine more or less profoundly altered. It also appears probable that the numerous ergot substances investigated by Jacobj (Chem. Zentr. 1897, i. 483, 1059) are mixtures (Kraft, Arch. Pharm. 244, 366; Barger and Carr, Chem. Soc. Trans. 91, 338).

The following substances were isolated by Kraft (*l.c.*): a phytosterol, *ergosterol*, which was first noted in 1869 by Ludwig (Arch. Pharm. 137, 36), and subsequently investigated by Tanret (Compt. rend. 108, 98); two alkaloids: *ergotinine* and *hydroergotinine*, which is isomorphous with and more soluble than ergotinine; a crystalline δ-lactonic acid, *secalonic acid* $C_{14}H_{14}O_6$, m.p. 244°, and the corresponding hydroxy acid, and another acid formed from this by loss of carbon dioxide; *aminosecalesulphonic acid* (Kobert's ergotic acid)

$$NH_2 \cdot C_{15}H_{27}O_{15} \cdot SO_3H;$$

betaine, choline, and mannitol.

Kraft's hydroergotinine, which corresponds to Tanret's amorphous ergotinine, was obtained in a high state of purity by Barger and Carr (*l.c.*) by recrystallising its salts. These investigators have given the name *ergotoxine* to this alkaloid.

To obtain ergotinine, the drug is extracted with 86 p.c. alcohol. The residue, after the removal of the spirit by distillation, separates into three parts: a fatty layer, an aqueous extract, and a resinous precipitate. The precipitate and the fatty layer are extracted with ether and the ethereal solution is shaken with dilute sulphuric acid which takes up the alkaloid as sulphate. The salts of the ergot

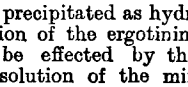
alkaloids are very slightly soluble in water and the slight solubility of the chloride and especially the bromide may be used as a means of purification. The residue left on evaporation of the alcoholic extract is treated with light petroleum to remove fat and oily matter; it is then dissolved in ethyl acetate and shaken with citric acid solution. Sodium bromide is added and the alkaloids are precipitated as hydrobromides. A rough separation of the ergotinine from the ergotoxine can be effected by the repeated shaking of the solution of the mixed hydrobromides in dilute caustic soda solution with ether. In this way the ergotinine is removed first. The base is then crystallised from alcohol, leaving ergotoxine in the mother liquor. Ergotinine crystals consist of long needles which, on heating, melt with decomposition about 220°, the exact point depending on the rate of heating. Analysis leads to the formula $C_{35}H_{39}O_5N_5$.

To prepare ergotoxine, the caustic liquor from which the ergotinine has been extracted is neutralised, rendered alkaline again with sodium carbonate and extracted with ether. The residue, after evaporation of the ether, together with that from the ergotinine mother liquors, is dissolved in 80 p.c. alcohol, and a slight excess of phosphoric acid in alcohol is added. After keeping for a few days, ergotoxine phosphate crystallises out and is recrystallised from alcohol. Obtained in this way, ergotoxine forms a light white powder which, when heated, softens at about 155° and gradually melts at 162°–164°. Analysis agrees with the formula $C_{35}H_{41}O_6N_5$. Ergotoxine can be converted by loss of water into ergotinine: for example, by boiling a solution of the former with methyl alcohol or by the action of acetic anhydride.

The colour reaction for ergotinine, described by Tanret, obtained by the addition of concentrated sulphuric acid to a solution of ergotinine in ether or in ethyl acetate, when a transitory orange colouration, changing to blue, appears; and also the colour reaction described by Keller, which occurs when anhydrous ferric chloride is added to ergotinine in concentrated sulphuric acid, in which case change of colour takes place from pale yellow to orange, crimson, green, and finally dark blue, are both given by ergotoxine and with the same intensity. Although ergotoxine is amorphous, it yields crystalline salts, whilst the salts from the crystalline ergotinine have only been obtained in an amorphous condition. Barger and Ewins (Chem. Soc. Trans. 97, 284) show that ergotoxine contains a carboxyl group and that ergotinine is its lactone (or lactam). On destructive distillation both ergotoxine and ergotinine yield a small quantity of *iso*butyrylformamide $CHMe_2{\cdot}CO{\cdot}CO{\cdot}NH_2$.

All the physiological effects described as characteristic of ergot, the alkaloid ergotoxine produces in very small dosage: (*a*) the effects ascribed by Kobert to sphacelinic acid, and by Jacobj to sphacelotoxin, viz. ataxia, dyspnœa, salivation, gastro-intestinal irritation, and gangrene; and (*b*) the stimulant effect on plain-muscular organs—in particular the arteries and the uterus—and the subsequent selective sympathetic motor paralysis given by many ergot preparations (Barger and Dale, Bio-Chem. J. 2, 240).

Ergotinine, however, when uncontaminated with ergotoxine, has apparently no physiological activity (Barger and Dale, Arch. Pharm. 244, 554).

In addition to the complex physiologically active alkaloid, ergotoxine, there are present in ergot other simpler bases possessing physiological action. Such bases are derived from amino-acids by the elimination of carbon dioxide and are generally formed in putrefaction. The first markedly active base of this class, *p-hydroxyphenylethylamine*, was isolated from the aqueous extract of ergot by Barger (Chem. Soc. Trans. 95, 1123). It is formed from tyrosine during putrefaction, but it appears to be present in fresh ergot and not merely to be formed by putrefaction. It is the chief pressor constituent of most aqueous ergot extracts but does not produce contraction of the isolated uterus of the non-pregnant cat. This substance is manufactured by Burroughs, Wellcome & Co. under the name 'tyramine.' Its physiological action has been described by Dale and Dixon (J. Physiol. 39, 25). A third active principle has been discovered in ergot by Barger and Dale (Chem. Soc. Trans. 97, 2592) and simultaneously by Kutscher (Zentr. Physiol. 24, 163). Barger and Dale proved this compound to be 4-*β-aminoethylglyoxaline* (*β-iminazoylethylamine*)  , a base previously obtained by the putrefaction of histidine (Ackermann, Zeitsch. physiol. Chem. 65, 504). Ackermann and Kutscher, however, consider it closely related but not identical with 4-*β*-aminoethylglyoxaline on account of differences in the physiological action of the two bases (Zeitsch. Biol. 54, 387). The physiological activity of this compound is very great, and the presence of this constituent accounts for the intense activity exhibited by some ergot extracts in producing contraction of the isolated non-pregnant uterus of the cat. A third active principle of this class has been found in ergot by Engeland and Kutscher (Zentr. Physiol. 24, 479). This is *agmatine* $NH_2{\cdot}C(:NH){\cdot}NH{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2$ which was previously discovered in herring roe by Kossel (Zeitsch. physiol. Chem. 66, 257). The action of this compound on the uterus is similar to that of 4-*β*-aminoethylglyoxaline.

The phytosterol in spurred rye, ergosterol, has the formula $C_{27}H_{42}O,H_2O$. It loses a molecule of water at 105°, and melts at 165°. When anhydrous, it quickly absorbs moisture from the air. It is accompanied in ergot by a similar crystalline substance *fongisterol*

$$C_{25}H_{40}O,H_2O,$$

m.p. 144°, a lower homologue of ergosterol (Tanret, Compt. rend. 147, 75).

Other pure substances which have been isolated from ergot are: uracil and succinic acid (Engeland and Kutscher, Zentr. Physiol. 24, 589), *iso*amylamine (Barger and Dale, Proc. Physiol. Soc., May 15th, 1909), putrescine and cadaverine (Rieländer, Sitzungsber. Ges. Naturw. Marburg, No. 7, 1908), leucine and aspartic acid of which Vahlen's 'clavine' (Arch. exp. Path. Pharm. 55, 131) is chiefly composed (Barger and Dale, Bio-Chem. J. 2, 295).

Tanret (Compt. rend. 149, 222) discovered in ergot a new base containing sulphur *ergothionine*

$$C_9H_{15}O_2N_3S,2H_2O_2$$

m.p. 290° (decomp.), which occurs to the extent of 0·1 p.c.

Ergot oil is dark brown in colour with a slightly irritant taste. Examined by Rathje (Arch. Pharm. 246, 602), its percentage composition was found to be oleic acid, 68; hydroxyoleic acid, 5; unsaponifiable matter, 0·35; inorganic matter, 0·2; alkaloid, 0·6; glycerol, 7·5.

Ergotismus or ergot-poisoning has occurred from time to time owing to the use of flour contaminated with ergot, and on this account a chemical examination of flour or bread for ergot is sometimes required. The methods employed depend chiefly on the recognition of the colouring matter of the fungus (*v.* Boettger, Chem. Zentr. [3] 2, 624; E. Hoffmann, Pharm. Zeit. 23, 576, 726, and 742; Stoddart, Pharm. J. [3] 10, 194; Wolff, Pharm. Zeit. 23, 532, and 694; Petri, Zeitsch. anal. Chem. 18, 211; Poehl, Ber. 16, 1975; Palm, Zeitsch. anal. Chem. 22, 319; Lauck, Lands. Versuchs-Stat. 1893, 305).

(For a method of evaluation of ergot of rye, *see* Beckurts and Grothe, Zeitsch. anal. Chem. 1899, 125; and Musset, Chem. Zentr. 1899, ii. 323.) A. S.

ERGOTIC ACID *v.* ERGOT OF RYE.

ERGOTINE *v.* ERGOT OF RYE; also VEGETO-ALKALOIDS.

ERGOTININE *v.* ERGOT OF RYE; also VEGETO-ALKALOIDS.

ERICA B *v.* PRIMULINE.

ERICOLIN is found in several plants belonging to the order *Ericaceæ*, especially in the herb of the marsh wild rosemary, *Ledum palustre* (Linn.) (Rochleder and Schwarz, Annalen, 84, 368), less abundantly in the common heath or ling, *Calluna vulgaris* (Salisb.) (Rochleder, *ibid.* 354), in *Rhododendron ferrugineum* (Linn.) (Schwarz, *ibid.* 361), and in the red bearberry, *Arctostaphylos Uva-ursi* (Spreng.) (Kawalier, Sitz. W. 9, 29).

To prepare it from *L. palustre*, the chopped leaves are thrown into boiling water and boiled for several hours. The filtrate obtained after adding basic lead acetate to the liquid is evaporated in a retort to one-third of its bulk. In Thal's modification of this process (Ber. 16, 1502), the liquid is concentrated *in vacuó*, the separated lead salt filtered off, and the liquid freed from lead by hydrogen sulphide. The filtrate is then evaporated to a syrup, and the ericolin dissolved out by anhydrous ether alcohol. The substance left on evaporating this solvent is repeatedly dissolved in a mixture of ether and alcohol till it no longer leaves any residue (Rochleder and Schwarz).

On heating the mother liquor obtained in the preparation of arbutin from the leaves of red bearberry with dilute hydrochloric or sulphuric acid, ericolin is deposited as a resinous precipitate, which may be purified by solution in alcohol and precipitation by water (Kawalier).

Rochleder and Schwarz, after deducting 10·6 p.c. ash, found ericolin to contain 51·71 p.c. carbon and 7·19 hydrogen, whence they deduced its formula to be $C_{34}H_{56}O_{31}$ (51·00 C and 7·00 H).

Thal (*l.c.*), after separating an admixed substance (containing 57·5 p.c. carbon and 7·29 hydrogen), which was insoluble in ether alcohol, from ericolin, assigned to the latter body the formula $C_{28}H_{24}O_{3}$, but subsequently altered it to $C_{28}H_{30}O_{3}$ to explain the decomposition equations of the substance. Ericolin, as prepared by Thal, is a brown-yellow, odourless, *hygroscopic*, *bitter* substance decomposing even below 100°. It is decomposed by water. By extracting successively with benzene, chloroform, and a mixture of ether and alcohol, different substances go into solution; it appears that the ericolin is thus broken up into a sugar and ericinol. With dilute sulphuric acid warmed to 100°, a sugar and a resinous brown-yellow viscid mass, hydroericinol, are produced. An analysis of the latter body gave numbers corresponding with the formula $x(C_6H_{12}O_2)$, subsequently modified to $x(C_5H_{10}O_2)$.

The equations representing these decompositions are as follows:—

$$\underset{\text{Ericolin.}}{C_{28}H_{30}O_3}+4H_2O=\underset{\text{Ericinol.}}{C_6H_{12}O_6}+C_{20}H_{26}O$$

$$\underset{\text{Ericinol.}}{C_{20}H_{26}O}+7H_2O=2(\underset{\text{Hydroericinol.}}{C_{10}H_{20}O_4}).$$

Power and Tutin, however, could not isolate ericolin by Thal's process, and they found that ericinol was identical with furfural (Chem. Zentr. 1907, i. 916).

Thal also isolated ericolin from *Calluna vulgaris* (Salisb.), and recognised it by the smell of ericinol in many *Ericaceæ* and *Vaccinieæ*.

Kanger extracted ericolin from the leaves of the cowberry (*Vaccinium vitis idæa*) by means of ether alcohol. It was then purified by precipitating foreign substances with lead acetate, and removing excess of the latter with sulphuretted hydrogen. The substance so obtained was of a resinous nature, completely soluble in ether alcohol, and corresponded with the composition $C_{16}H_{25}O_{10}$ (Chem. Zeit. 1903, 27, 794). Ericolin is probably not a chemical individual, but consists of a mixture of glucoside-like substances.

Ericolin is poisonous towards many micro-organisms, particularly those belonging to the colon group, but has no action on acid-fast bacilli. Twort (Proc. Roy. Soc. 1909, B, 81, 248) has used it as a medium for the isolation and culture of human tuberculous bacilli from sputum.

ERIGERON CANADENSE is an oil consisting of a terpene boiling at 176°, which, when pure, has sp.gr. 0·850–0·870, and an optical rotation +52°. It is soluble in an equal volume of alcohol, and rapidly resinifies. The commercial oil has sp.gr. 0·8549–0·8963; optical rotation, +28° 48′ to 84·20°; and b.p. 172°–178° (Kepler and Pancoast, Amer. J. Pharm. 75, 216).

According to Rabak (Pharm. Review, 1905, 23, 81; 1906, 326), the oil obtained from the fresh herb (0·66 p.c.) is of a bright-yellow colour with a peculiar odour like that of caraway. On exposure to air, it deposits crystals, and a brownish resinous mass is formed. The oil from the dried herb (0·26 p.c.) was darker in colour, had a powerful aromatic odour, and gave no crystals when exposed to air. It also differed from the fresh herb oil in sp.gr., optical rotation, and other characteristics. In all probability, the terpeneol found in erigeron oil is a decomposition product. The oil absorbs two molecules of hydrochloric acid to form a solid dihydrochloride $C_{10}H_{16}.2HCl$, melting at 47°–48° (Beilstein and Wiegand, Ber. 15, 2854; Wallach, Annalen, 227, 292).

ERIOGLAUCINE. The trade name of the dyestuff obtained by condensing benzaldehyde-*o*-sulphonic acid with ethylbenzylanilinesul-

phonic acid (J. Soc. Chem. Ind. of Basle, Eng. Pat. 25128; Gnehm and Schüle, Annalen, 299, 347).

ERUCIC ACID $C_{22}H_{42}O_2$. A homologue of acrylic acid obtained, together with oleic acid, by the saponification of the fixed oil of white mustard. It was found together with behenic acid by Goldschmiedt (Sitz. W. 70, 451) in the oil expressed from black mustard, and by Fitz (Ber. 1871, 442) in the fat oil of grape seeds. It is best obtained by saponifying rape oil (from *Brassica campestris*, Linn.) with alcoholic potash, distilling off the alcohol and dissolving the acid liberated on the addition of sulphuric acid in three times its volume of 95 p.c. alcohol; on cooling to 0°, crystals of erucic acid separate out in an almost pure condition (Reimer and Will, Ber. 1886, 3320). It may be obtained by saponifying colza oil, freeing the erucic acid from arachidic acid by treatment with glacial acetic acid, in which the latter is insoluble (Ponzio, Gazz. Chim. ital. 1904, ii. 50). It is also present in cod liver oil (Bull, Ber. 1906, 3570).

Erucic acid crystallises in colourless needles, m.p. 34°; b.p. 281° at 30 mm. Heated with phosphorus oxychloride, it forms an anhydride $C_{44}H_{82}O_3$, an oil which may be crystallised in a freezing mixture. By treatment with nitrous acid, or better, by warming erucic acid with dilute nitric acid to the melting-point and then adding sodium nitrite, brassidic acid (brassic acid) is produced. This acid stands to erucic acid in the same relation as elaidic to oleic acid. Fused with potash, erucic acid yields aradic (arachidic) and acetic acids. Concentrated nitric acid converts erucic acid into brassilic acid ($C_{13}H_{24}O_4$), pelargonic acid, arachidic acid, and a small quantity of dinitrononane (Fileti and Ponzio, J. pr. Chem. [2] 48, 323), and concentrated sulphuric acid into behenolactone (Shukow and Schestakow, Chem. Zentr. 1908, ii. 1415). With hydriodic acid and amorphous phosphorus, it is converted into behenic acid (Goldschmiedt, J. 1876, 579). On treatment with phosphorus triodide, iodobehenic acid is obtained, which on treatment with alcoholic potash, yields *iso*-erucic acid, m.p. 54° (Ponzio, *l.c.*). Erucic acid is converted into behenic acid by heating with iodine in a sealed tube for 4 hours at 270° (Reychler, Bull. Soc. chim. [3] 1, 296). When bromine is added to erucic acid under water, a dibromide $C_{22}H_{42}Br_2O_2$ is produced. It crystallises from alcohol in small white nodular crystals, m.p. 42°–43°, and is reduced to erucic acid by sodium amalgam in alcoholic solution. Its barium and lead salts $(C_{22}H_{41}Br_2O_2)_2Ba$ and $(C_{22}H_{41}Br_2O_2)_2Pb$ are white, viscid, easily decomposable precipitates (Otto, Annalen, 127, 182; 135, 226). Erucic acid dibromide heated in sealed tubes to about 145° for 7–8 hours, with 4 or 5 mols. potassium hydroxide in alcoholic solution, yields the potassium salts of behenolic acid

$$C_{22}H_{40}O_2(=C_{22}H_{42}Br_2O_2-2HBr)$$

(Holt, Ber. 1892, 961). Behenolic acid, on treatment with zinc-dust and acetic acid, yields brassidic acid and not erucic acid. At ordinary temperatures, only 1 mol. of hydrobromic acid is abstracted by potash in alcoholic solution; monobromerucic acid $C_{22}H_{41}BrO_2$ is formed, with rise of temperature and separation of potassium bromide. On diluting the solution with water and adding hydrochloric acid, the acid separates as an oil which soon solidifies. It melts at 33°–34° and remains liquid for a long time. It is heavier than water, and insoluble therein, but dissolves readily in alcohol and ether. It unites with bromine, forming a dibromide $C_{22}H_{41}BrO_2{\cdot}Br_2$, which melts at 31°–32°, and forms amorphous viscid salts.

When erucic acid dibromide is triturated with water and an excess of silver oxide, and heated until it turns brown and evolves hydrogen bromide, the mass, on boiling with water, yields a yellow oil which is a mixture of liquid hydroxyerucic acid $C_{22}H_{42}O_3$ and dihydroxybehenic acid $C_{22}H_{44}O_4$. The latter partially crystallises out on long standing. For complete separation, the washed oil is saponified with baryta water; the precipitate is exhausted with ether and the dissolved barium hydroxyerucate is decomposed by hydrochloric acid. The hydroxyerucic acid, which separates as a colourless oil, is purified from alcohol. It is viscid, lighter than water, insoluble therein, but miscible in all proportions with alcohol and ether. Its salts $C_{22}H_{41}O_3M$ are amorphous. All excepting those of the alkali metals and barium are insoluble in water. Hydroxyerucic acid may also be formed from monobromerucic acid by the action of silver oxide. Boiled with potash lye, it is converted into dihydroxybehenic acid (Haussknecht, Annalen, 163, 40). Dihydroxybehenic acid, m.p. 132°–133°, is also obtained by the oxidation of erucic acid with potassium permanganate (Hazura and Grüssner, Monatsh. 9, 947). Sodium erucate $C_{22}H_{41}NaO_2$ is soluble in alcohol, and gives precipitates of lead and barium erucates on the addition of an alcoholic solution of the acetates of these metals. The silver salt is a curdy precipitate, which becomes coloured on exposure to light.

Ethyl erucate $C_{22}H_{41}(C_2H_5)O_2$ is a colourless oil boiling above 360° without decomposition. The amide $C_{22}H_{41}O(NH_2)$, m.p. 84° (Reimer and Will, *l.c.*), m.p. 78°–79° (Krafft and Tritschier, Ber. 1900, 3580), and the anilide, m.p. 55°, are crystalline bodies readily soluble in ether or benzene, sparingly soluble in alcohol.

ERUCIN. A crystalline body said to exist in white mustard seed. It is insoluble in water, sparingly soluble in alcohol, easily in ether or in oils (Simon, Pogg. Ann. 64, 593).

Dierucin $C_3H_5OH(C_{22}H_{41}O_2)_2$. When rape oil is allowed to stand for a long time, a yellowish tallow-like deposit is found frequently in the casks. This, by repeated solution in ether and subsequent addition of alcohol, may be obtained in silky needles. Dierucin melts at 47° and is readily soluble in ether and light petroleum, insoluble in cold but soluble in hot alcohol. A trierucin could not be separated from rape oil, but was obtained by heating dierucin and erucic acid at 300°, m.p. 31° (Reimer and Will, *l.c.*) (*v.* OILS AND FATS).

ERYTHRIN, *Erythric acid, Erythrinic acid, Erythrolecanoric acid* $C_{20}H_{22}O_{10},H_2O$, is a constituent of most lichens from which archil is prepared. It was discovered by Heeren (Schweigger's Jour. f. Chem. 59, 513) in *Rocella tinctoria* (D. C.), from which lichen and several others of the same genus it may be extracted by boiling water, or better with milk of lime (*cf. also*

Kane, Stenhouse, and Hesse (*l.c.*); Schunck, Annalen, 61, 69; De Luynes, Annalen de Chim. [4] 2, 385; Menschutkin, Bull. Soc. chim. [2] 2, 424).

The method adopted by Stenhouse to prepare this substance from the *Rocella fuciformis* is as follows (Annalen, 68, 72, and 149, 290). Three pounds of the lichen are macerated for 20 minutes in a milk of lime made by shaking ½ lb. of lime in 3 gallons of water, and the product filtered by means of a bag filter. The clear liquid, as it passes through, is immediately precipitated with hydrochloric acid, as prolonged contact with the lime decomposes part of the erythrin. The crude erythrin collected on bag filters is freed from acid and calcium chloride by stirring it up once or twice with a considerable quantity of water and again collecting.

Erythrin forms small colourless needles, melting at 148° (Hesse, Ber. 1904, 37, 4693), and not at 164°, as stated by Ronceray (Chem. Zentr. 1904, ii. 1504), and is sparingly soluble in water, easily soluble in alcohol, ether, and alkalis. Alcoholic ferric chloride gives a purple-violet colouration, which passes to brownish-red on addition of excess of the reagent.

When boiled with water, erythrin gives (*a*) *orsellinic acid* and (*b*) *picro-erythrin* (Schunck, Annalen, 61, 65)

$C_{20}H_{22}O_{10}+H_2O=(a)\ C_8H_8O_4+(b)\ C_{12}H_{16}O_7$;

whereas by boiling with alcohol, picroerythrin and *orsellinic acid ethyl ester* (*c*) are produced (Heeren, *l.c.*; Kane, Annalen, 39, 25)

$C_{20}H_{22}O_{10}+C_2H_5OH=(c)\ C_8H_7(C_2H_5)O_4+C_{12}H_{16}O_7$.

With amyl alcohol, a similar reaction occurs with formation of (*d*) *amylorsellinate* and picroerythrin (Hesse, Annalen, 139, 22)

$C_{20}H_{22}O_{10}+C_5H_{12}O=(d)\ C_8H_7O_4{\cdot}C_5H_{11}+C_{12}H_{16}O_7$.

On the other hand, excess of lime water (Lamparter, Annalen, 134, 255) gives orcin, CO_2, and erythrite

$C_{20}H_{22}O_{10}+2H_2O=2C_7H_8O_2+CO_2+C_4H_{10}O_4$.

Tribromerythrin $2C_{20}H_{19}Br_3O_{10},3H_2O$ (Hesse, Annalen, 117, 310; and *ibid.* 139, 32) consists of white crystalline spherules which cake together a little above 100° and melt at 139°. Boiled with alcohol, it is resolved into *ethyldibromorsellinate* and *brompicroerythrin*.

Picroerythrin or *erythro-orsellinic acid*

$C_{12}H_{16}O_7,3H_2O$,

forms colourless prisms, melts at 158°, is readily soluble in hot water, and gives with ferric chloride a purple-violet colouration. It appears to be most readily obtained pure by Hesse's method of boiling erythrin with amyl alcohol (*l.c.*).

Digestion with hot baryta water converts picroerythrin into CO_2, orcin, and erythrite

$C_{12}H_{16}O_7+H_2O=CO_2+C_7H_8O_2+C_4H_{10}O_4$.

The experiments of de Luynes, Menschutkin, and Hesse have confirmed the view first put forward by Berthelot, that erythrin is the *monolecanoric ester* (1), and picroerythrin the *monoorsellinic ester* of *erythrite* (2).

According to Hesse (Ber. 1904, 37, 4693), erythrin contains a free carboxyl group, and must therefore be represented as follows:—

$C_4H_6(OH)_2{\cdot}O{\cdot}C_6H_2(OH)CO{\cdot}O{\cdot}C_6H_2(OH)COOH$.
$\quad\quad\quad

Hardy (Bull. Soc. chim. [2] 26, 39), Harnack and Zabrocki (Ber. 15, 2623), Harnack (Ber. 16, 87).

Commercial erythrophleïne hydrochloride is a bright-yellow amorphous hygroscopic powder, soluble in water. The free base is precipitated from the solution of the hydrochloride by alkalis. The hydrochloride is very poisonous, but only acts as digitaline, not at all as picrotoxine. When heated with 38 p.c. hydrochloric acid in a reflux apparatus, it splits up into erythrophleïc acid and methylamine (Harnack, Arch. Pharm. 1896, 234, 561). Erythrophleïc acid readily forms an anhydride $C_{27}H_{53}O_7$ or $C_{27}H_{40}O_7$. The salts of the acid are amorphous (*v.* VEGETO-ALKALOIDS).

ERYTHROSIN (*Tetraiodofluorescein*)

$C_{20}H_8O_5I_4$

is prepared by electrolysing a mixture of fluorescein (1 part) and finely powdered iodine (1·5 parts) in soda solution. The vessel is provided with a diaphragm, and the fluorescein mixture occupies the anode space, whilst a dilute solution of soda or sodium hydroxide forms the kathode liquid (D. R. P. 108838, 1899; Chem. Zentr. 1900, i. 1176; *cf. also* Frdl. 1877–87, 315).

The commercial product is a red-brick powder dissolving in dilute alkalis without any marked fluorescence. It can be purified by dissolving in aqueous ether, filtering and shaking with dilute sodium hydroxide. The sodium salt is precipitated by the addition of strong alkali, and, after filtering, washing, and recrystallisation from alcohol, it is dissolved in water, and the free erythrosin is liberated by treatment with hydrochloric acid (Mylius and Foerster, Ber. 1891, 24, 1482). When pure, it is of a lighter colour than the impure product, almost insoluble in absolute ether, benzene, or chloroform, but more readily so in acetone, alcohol, and aqueous ether. The colour of erythrosin fades under the influence of light and of hydrogen peroxide, particularly in the presence of potassium hydroxide (Zeitsch. Farbenindustr. 1908, 7, 299). Light also causes it to act hæmolytically in photodynamic reactions (Sacharow and Sachs, Chem. Zentr. 1905, i. 1420).

Erythrosin considerably enhances the action of light in its influence on bacteria (Mettler, Chem. Zentr. 1905, ii. 1037; Huber, *ibid.* 1906, i. 148; Sacharow and Sachs, *l.c.*). Erythrosin is employed in the cotton and paper industries; and Thouert (Compt. rend. 1909, 148, 36) has attempted to apply it to colour photography, but with little success so far (*cf. also* Stark, Physikal. Zeitsch. 1907, 8, 248); it has also been used as a sensitiser in photo-electric experiments (Schlenderberg, J. Phys. Chem. 1908, 12, 574) and as an indicator in analysis (Mylius and Foerster, *l.c.*; J. Amer. Chem. Soc. 1899, 21, 359).

Erythrosin is often mixed with rose Bengal (tetraiodochlorofluorescein) to suppress its fluorescence, and with common salt to increase its solubility. The former mixture is often used in France to colour foodstuffs, but the presence of rose Bengal in erythrosin is forbidden in America. Jean (J. Soc. Chem. Ind. 1908, 70) gives a method for testing and estimating rose Bengal in erythrosin.

Silver erythrosin, which is of an intense blue colour, is prepared by dissolving 1 gram of erythrosin in 400 c.c. water, adding 7·1 c.c. of a 10 p.c. solution of potassium bromide, and then 12 c.c. of a 10 p.c. silver nitrate solution. It forms a colloidal solution which becomes 'ripened' on warming or standing for a few days, depositing a very fine sediment which has a pure blue colour in transmitted light (Lüppo-Cramer, Zeitsch. Chem. Ind. Kolloide, 1907, i. 227; 1908, 2, 325).

The sodium or potassium salt is sometimes known as Erythrosin B, Pyrosin B, Iodeosin Dianthine B, Eosin J, &c.

ERYTHROXYANTHRAQUINONE $C_{14}H_8O_3$ is produced, along with an isomeric hydroxyanthraquinone, by the action of phthalic anhydride on phenol, in presence of sulphuric acid, $C_8H_4O_3+C_6H_6O=H_2O+C_{14}H_8O_3$. Salicylic acid, anisole, and even anisic acid behave in the same way as phenol. The two hydroxyanthraquinones are separated by boiling with water and barium carbonates; erythroxyanthraquinone is unaltered by this treatment, whereas in the case of the isomer a soluble barium compound is formed.

Erythroxyanthraquinone may also be prepared from aminoanthraquinone, dissolved in acetic acid to which a little sulphuric acid has been added, by adding potassium nitrite till the solution becomes yellow. After a short time, on adding water and boiling, yellow flakes of erythroxyanthraquinone separate, and increase as the acetic acid evaporates (D. R. P. 97688; Rower, Ber. 1882, 15, 1793; Perger, J. pr. Chem. [2] 18, 147).

It is also formed by oxidising the amino-salt with fuming sulphuric acid (D. R. P. 67063; Frdl. iii. 203); or by heating erythroxyanthraquinone acid $C_{15}H_8O_5$ at 270° (Birnkow, Ber. 1887, 20, 2438), and by heating anthraquinone-α-monosulphonic acid with a mixture of alkali hydroxide and a salt of an alkaline earth metal under pressure (Fr. Pat. 336867; J. Soc. Chem. Ind. 1904, 438; *ibid.* 1905, 841).

Erythroxyanthraquinone crystallises from alcohol in groups of pomegranate-yellow needles, more soluble in hot than in cold alcohol. It melts at 173°–180° (Baeyer and Caro), at 190° (Liebermann), at 191° (Römer). It begins to sublime at 150°, and condenses to form fine needles, reddish-yellow in colour, like alizarin. It is almost insoluble in dilute ammonia, and only slightly soluble in strong ammonia. With lime or baryta water it gives a dark-red, almost insoluble lake, decomposable by carbon dioxide. The absorption spectrum of a sulphuric acid solution of erythroxyanthraquinone differs from that of its isomeride, hydroxyanthraquinone; the latter body is also more easily converted into alizarin by fusion with caustic potash than the former (Baeyer and Caro, Ber. 7, 968).

Nitric acid oxidises ethythroxyanthraquinone to phthalic acid.

When sodium erythroxyanthraquinone sulphonate is heated with bromine and water at 120°–123°, *2:4-dibromo-1-hydroxyanthraquinone* is formed, crystallising in reddish-yellow needles, m.p. 233°. When heated with *p*-toluidine at 80°–100°, this bromine derivative loses the

bromine atom in the -4- position, and is converted into bromoquinizarin blue

$$C_6H_4\langle\begin{matrix}CO\\CO\end{matrix}\rangle C_6\cdot HBr(OH)(NHC_7H_7)$$

which crystallises in blue needles, giving a green colouration with sulphuric acid (D. R. P. 127532, 1902).

Erythroxyanthraquinone forms an acetate $C_{18}H_{10}O_4$, yellow needles, m.p. 176°–179° (Liebermann and Hagen, Ber. 1882, 5, 1804).

The constitution of erythroxyanthraquinone has been established by Liebermann (Ber. 10, 611; 11, 1611), who synthesised it from a reduction product of quinizarin, hydroxyhydroanthranol $C_6H_4\langle\begin{matrix}CH_2\\CH(OH)\end{matrix}\rangle C_6H_3(OH)$, in which the hydroxyl-group in the benzene nucleus occupies the ortho- position. Frande (Ber. 12, 237) was also able to show that in methylhydroxyanthraquinone, a derivative of ordinary hydroxyanthraquinone, the hydroxyl-group was in the para- position, and hence, in the isomeric erythroxyanthraquinone, the hydroxyl- group must be in the ortho- position with regard to the ketone group. Erythroxyanthraquinone is therefore o-hydroxyanthraquinone (*v.* ALIZARIN AND ALLIED COLOURING MATTERS).

ESERINE or PHYSOSTIGMINE

$$NHMe\cdot CO\cdot NHC_{13}H_{15}N\cdot OH$$

(Herzig and Meyer, Monatsh. 1897, 18, 389; Heubner, Chem. Zentr. 1905, ii. 1111) is the most important of the alkaloids occurring in Calabar bean, in the seed of which it was first found by Jobst and Hesse, in 1864 (Annalen, 1864, 129, 115; Hesse, *ibid.* 1867, 141, 82).

It is present to the extent of about 0·18 p.c., and may be extracted by shaking the powdered seed with warm alcohol containing about 1 gram of tartaric acid per litre. The alcohol of the extract is distilled off and the residue is taken up with water, filtered to remove resinous matter and shaken with ether until the latter ceases to be coloured. The aqueous extract is then made alkaline with sodium bicarbonate and finally repeatedly shaken out with ether. On evaporation, the alkaloid separates in scaly crystals which may be purified by recrystallisation from ether.

Eserine forms thin rhomboidal, colourless lamellæ, m.p. 105°–106°, which gradually assume a rose tint and even a yellow colour when exposed to air. It is sparingly soluble in water, but readily so in alcohol, ether, chloroform, benzene, and carbon disulphide. Eserine is lævo-rotatory, its specific rotation varying between −82° and −120°, depending on the solvent employed (Petit and Polonowsky, Bull. Soc. chim. 1893, 9, 1008; *cf.* Orloff, Chem. Zentr. 1897, i. 1214).

When eserine is isolated in the form of its salicylate, the base liberated with sodium carbonate, extracted with ether, and finally allowed to crystallise from a mixture of benzene and petroleum, it separates in stout prisms, m.p. 86°–87°, $[\alpha]_D$ −75·8°. By recrystallising in the presence of a crystal of Petit and Polonowsky's modification, m.p. 105°–106°, it is completely converted into the latter, and has $[\alpha]_D$ −75·8°; the alkaloid is therefore dimorphous (Salway, Chem. Soc. Trans. 1910, 2151).

When eserine or its salts are distilled with caustic potash in a current of hydrogen, methylamine and carbon dioxide are amongst the products of decomposition, whilst the residual liquid contains *eseroline*, a colourless crystalline body, which turns red by the action of moisture. Eseroline is also formed, together with methyl carbamide, when eserine is heated in a sealed tube with alcoholic ammonia at 150°. When heated with aqueous potash in presence of air, eserine yields *rubreserine* $C_{18}H_{16}N_2O_2$, red needles, these, in alkaline solution, are gradually converted into *Eserine blue*, which, according to Ehrenberg (Chem. Zentr. 1894, ii. 439), is a true dye, colouring wool and silk without mordants. The constitution of eserine blue is not known. It is not poisonous, but it has a paralysing effect on the heart and central nervous system of the frog (Heubner, *l.c.*).

Salts of eserine. *Eserine salicylate* $C_6H_4(OH)CO_2H,C_{15}H_{21}O_2N_3$ forms slightly bitter, colourless, stout prisms, m.p. 180°–181° (Salway), sparingly soluble in water, in which it forms an acid solution, more readily soluble in alcohol and in chloroform.

Eserine metacresotate (*metahydroxytoluate*) $C_{15}H_{21}O_2N_3\cdot C_6H_3(OH)MeCO_2H$, m.p. 156°–167°, is prepared by mixing ethereal solutions of metacresotic acid and of eserine. *Eserine benzoate*, m.p. 115°–116°, and *eserine hydrogen citrate*, are prepared similarly. The two former are not deliquescent, and yield neutral aqueous solutions; whereas the latter, and also normal *eserine tartrate*, prepared by dissolving eserine in tartaric acid and crystallising over sulphuric acid, are very deliquescent (Petit and Polonowsky, *l.c.*). The *methiodide* forms deliquescent yellow prisms, m.p. 100° (decomp.), and the sparingly soluble picrate crystallises in feathery yellow needles, m.p. 114°. Eserine yields no definite aurichloride or platinichloride.

Eserine sulphate $(C_{15}H_{21}O_2N_3)_2H_2SO_4$ is prepared by adding a 10 p.c. sulphuric acid, drop by drop, to an ethereal solution of eserine until the newly formed salt no longer separates. After filtration, it is carefully dried at about 40°. It is a white or yellowish-white micro-crystalline powder, odourless, and having a bitter taste. It is readily soluble in water, alcohol, and in chloroform. Gold chloride solution, when added to the aqueous solution of the salt, gives a beautiful purple colour; whilst platinic chloride precipitates a yellowish-white salt. When evaporated with ammonia, the sulphate, like the salicylate, yields a bluish residue. If a little eserine sulphate is placed on a glass slip and moistened with water, and then a drop of sulphuric acid added, characteristic crystals of a sparingly soluble sulphate separate. This characteristic appearance is maintained for some time, but eventually the crystals become oily and then resinous (Reichard, Pharm. Zeit. 1909, 50, 375). Eserine and its salts turn red on treatment with alkali or on standing in solution, but the *sulphite* $C_{15}H_{21}O_2N_3,H_2SO_3$, the aqueous solution of which does not turn red, but remains colourless, has been prepared by Merck by treating a solution of eserine with sulphurous acid, and evaporating the mixture (D. R. P. 166310; J. Soc. Chem. Ind. 1906, 443). It is a white powder, readily soluble in water.

A derivative, the intensity of the fluorescence of which exceeds that of all known substances, is obtained by allowing an aqueous solution of physostigmine to stand for a few months until it has become deep blue, then adding phthalic acid. The substance forms dark-blue crystals with a blood-red fluorescence, and colours cotton, silk, alcohol, ether, &c., dark blue with no fluorescence. The aqueous solution, on the other hand, is colourless by transmitted light, but shows a beautiful red fluorescence by reflected light (Goubert, Compt. rend. 1909, 149, 852).

Eserine and its salts should be kept in amber-coloured, well-stoppered phials.

Test for eserine or its salts.—A small fragment (the size of a grain of sand) is placed in a porcelain capsule and dissolved in a drop or two of fuming nitric acid The dark-yellow solution formed on warming is evaporated with stirring; the residue, which is of a pure green colour, dissolves in water, strong alcohol, and in sulphuric acid to a clear green solution. 0·005 gram of the alkaloid can thus be detected. The green colouring matter has been termed *chloreserine* (Silva, Compt. rend. 1893, 117, 330; Formanek, Chem. Zentr. 1895, i. 1148; Richard, *l.c.*). When exposed to nitric acid fumes, the blue residue becomes violet-blue; and when dissolved in a drop of nitric acid it forms a beautiful reddish-violet solution, which soon changes to blood-red, and on standing or on dilution becomes greenish-yellow. Eserine reduces molybdic acid very slowly in the cold, but rapidly gives a blue colouration on warming (Reichard, *l.c.*). With ammonium selenite in concentrated sulphuric acid, eserine gives a lemon-yellow colouration, which becomes orange, and then paler after standing for 3 hours (Silva, Compt. rend. 1891, 112, 1266). Eserine can also be detected by means of the polarisation microscope (Kley, Rec. trav. chim. 1903, 22, 367). (For the estimation of eserine or physostigmine, *see* Heikel, Chem. Zentr. 1909, i. 949.)

Eserine and its salts are of considerable therapeutic value, being employed chiefly as a myotic to contract the pupil of the eye and to decrease intraocular pressure in glaucoma.

According to Pal (Chem. Zentr. 1900, ii. 1031), eserine forms an antidote to the poisonous effect of curare.

Bilateral antagonism exists between eserine and curare in their effect on muscle. Those muscles which, like the diaphragm, are last paralysed by curare are first set free again by the injection of eserine. The latter also stimulates the respiratory centre (Rothberger, Pflüger's Archiv. 1901, 87, 117).

(For other investigations on the physiological effect and use of eserine or physostigmine, *see* Matthews and Brown, Amer. J. Physiol. 1904, 12, 173; Edmund and Roth, *ibid.* 1908, 23, 28, 46; Joseph, *ibid.* 1909, 23, 215; Anderson, J. Physiol. 1905, 33, 414; Magnus, Pflüger's Archiv. 108, 1; Kress, *ibid.* 109, 608; Modrakowski, *ibid.* 118, 52; Ungar, *ibid.* 119, 339; Harnack, Chem. Zentr. 1908, ii. 338; Winterberg, *ibid.* i. 750; Loewi and Mansfeld, *ibid.* 1910, i. 941; Pewsner, Biochem. Zeitsch. 1907, 2, 339.) (*V.* VEGETO-ALKALOIDS.)

ESPARTO, *Stipa marcrochloa* (*tenacissima*) (Linn.). This grass is a native of Spain, Portugal, Greece, and North Africa. It is largely used as a raw material for paper making, having been introduced into this country by Routledge. For this purpose it possesses many advantages, as it grows abundantly without cultivation, is easily harvested, yields a large percentage of cellulose of high quality with comparatively simple treatment.

Of the various kinds known to commerce, such as Spanish, Tripoli, Arzen, Oran, Sfax, Gabes, &c., the first-named is preferred by paper makers, as it yields more and better fibre. It therefore commands a higher price.

To give some idea of the importance of esparto as a paper-making material, it may be mentioned that the annual imports into the United Kingdom are between 200,000 and 300,000 tons.

It is also used for the purpose of making coarse mats and ropes (*v.* Spon's Enc. of the Industrial Arts).

Esparto arrives in this country firmly pressed into bales. The first operation which it undergoes in the paper mill is that of 'dry-picking,' in contradistinction to a subsequent process known as 'wet-picking.' The grass is spread out on tables covered with coarse wire cloth, and any root ends, weeds, &c., which may have found their way into the bales through imperfect gathering are picked out. Any sand or dirt escapes through the wire cloth. The removal of dirt can be more completely effected by machinery. For this purpose the grass is fed into a mechanical duster or willow, where it receives a violent shaking, the dirt being loosened and removed. The cleaned esparto is then fed into 'vomiting' boilers, where it is treated with caustic soda solution at pressures varying from 10 to 40 lbs. per sq. inch for from 3 to 5 hours. The amount of soda required is about 17 lbs. of 60 p.c. caustic soda per cwt., but it varies with the quality of the grass, the form of boiler, the pressure at which it is boiled, and the time allowed. When the boiling is completed, the liquor is run away, evaporated to dryness, and ignited, and the alkali recovered in the form of carbonate. This is dissolved in water, converted into caustic by means of lime, and is again available for use.

The boiled grass is washed once or twice in the boiler, and then subjected to the 'wet-picking' process, whereby any unboiled portions are removed. The process is being gradually abandoned in favour of what is known as the 'presse-pâte' system, which consists in purifying the pulp by passing it when bleached through a series of strainers and knotters. It is then made into a coarse web of pulp on the 'presse-pâte,' which may be described as a paper machine without the drying cylinders.

The subsequent treatment of esparto does not differ essentially from that of other fibres, and need not be particularly described.

The haulms (really leaves) of esparto vary in length from 0·3 to 0·5 m., the mean thickness being about 1·5 mm.; the individual fibres are 100–400 mm. long, and 0·009–0·5 mm. thick.

The fibres possess, owing to their fineness and their tendency to curl, considerable 'felting' properties. Paper made from esparto is soft to the touch, 'bulks' well, and at the same time is strong.

Esparto fibre can be recognised in a paper

by the fact that when boiled with a solution of aniline sulphate a rose-pink colour is developed. A similar colour is produced with straw cellulose, but of a paler shade. With iodine and sulphuric acid the wall of the actual bast-fibre assumes a rusty colour, showing that it is not composed of cellulose; with aniline sulphate (cold) it is stained yellow; and with phloroglucinol and hydrochloric acid a crimson colour is assumed, thus demonstrating the presence of bodies characteristic of lignified walls. They can be distinguished by the size and shape of the peculiar serrated epidermal cells, which are to be seen when the commercial fibre is examined under the microscope.

Moreover, esparto pulp always has a number of the short conical, often hooked, hairs which line the inner (upper) surface of the 'rolled' leaf, and which serve to distinguish it from straw; the outer (lower) surface of the leaf is glabrous.

The chemical characteristics of esparto are those of the ligno-celluloses and the pecto-celluloses, the latter predominating.

Its composition is shown by the following analyses (Hugo Müller):—

	Spanish	African
Cellulose . .	48·25	45·80
Fat and wax. .	2·07	2·62
Aqueous extract .	10·19	9·81
Lignin and pectous substances .	26·39	29·30
Ash . . .	3·72	3·67
Water . . .	9·38	8·80
	100·00	100·00

The names 'esparto,' 'sparto,' and 'alfa' ('halfa'), are also given to the leaves of another grass, *Lygeum spartum* (Loefl.), which likewise grows in Spain and North Africa. These leaves are used as an inefficient substitute for those of *stipa*. Microscopically they differ, in that the hairs have a considerable lumen, and are usually blunt-ended; the epidermis has peculiar little rounded silica cells; and the ribs of bast fibres are isolated (not linked together to form a continuous band, as in *Stipa*).

ESTERIFICATION. The reaction between an acid and a monohydric alcohol appears, at first sight, to be exactly analogous to the neutralisation of an acid by a monoacid base: the equations are:

$$CH_3{\cdot}CO{\cdot}OH+C_2H_5{\cdot}OH=CH_3{\cdot}CO{\cdot}OC_2H_5+H_2O$$

and

$$CH_3{\cdot}CO{\cdot}OH+NaOH=CH_3{\cdot}COONa+H_2O.$$

The product formed in the second reaction is a metallic salt, and that in the first reaction is termed an alkyl salt or more commonly an *ester*. The esters can be regarded as metallic salts in which the metallic radicles have become replaced by alkyl- groups. Corresponding with mono-, di-, and trivalent-metallic radicles are the mono-, di-, and trivalent hydrocarbon radicles, methyl CH_3-, ethyl C_2H_5-, propyl C_3H_7-, &c., methylene $CH_2=$, ethylidene $C_2H_4=$, &c. glyceryl $C_3H_5\equiv$, &c. The process of the conversion of an acid into its alkyl-salts is usually termed *esterification*, and is the common method by means of which esters are prepared. Although this reaction appears to be similar to the process of neutralising an acid by means of an alkali, there are two important points of difference.

1. The reaction between an acid and an alkali in aqueous solution is instantaneous, whereas the reaction between an acid and an alcohol is usually slow, and lends itself readily to study as a time reaction.

2. In the process of neutralisation between strong acids and strong alkalis, the reaction proceeds to completion when equivalent quantities of acid and alkali are used; but when equivalent amounts of acid and alcohol are brought together, complete conversion into ester and water never takes place. The reaction begins slowly and proceeds until a state of equilibrium is established. The rate at which the reaction proceeds, and the final equilibrium depend upon the specific acid and alcohol employed and upon the temperature. The process of esterification is a typical balanced or reversible reaction:

$$R{\cdot}CO_2H+R'{\cdot}OH \rightleftarrows R{\cdot}CO_2R'+H_2O$$

as the water formed in the process of esterification can hydrolyse the ester to a certain extent. This reaction is one of the best to study in order to illustrate the effects of mass action.

The reaction between acetic acid and ethyl alcohol was studied by Berthelot and Pean de St. Gilles, in 1862; they showed that working with equivalent quantities of alcohol and acid, equilibrium is reached when 66 p.c. of the reacting compounds have been transformed into ester and water. They were able to show that, by working with an excess of alcohol, a higher percentage of the acid can be transformed, as illustrated by the following numbers:—

Equivalents of alcohol for 1 equivalent of acid	0·2	0·5	1·0	1·5	2·0	4·0	12	50
p.c. of acid transformed into ester	19	42	66·5	78	83	88	93	100

According to Guldberg and Waage's law of mass action formulated in 1867, the rate of chemical reaction is proportional to the concentrations (molecular) of the reacting substances, and to a constant which is characteristic of the reaction and retains the same value provided the temperature is constant. In the balanced reaction:

$$CH_3{\cdot}CO_2H+EtOH \rightleftarrows CH_3{\cdot}CO_2Et+H_2O$$

the direct reaction proceeds at a rate which can be denoted by $K.a.b$, where K is the specific constant for this reaction, and a and b are the concentrations of the acid and alcohol at the time of measuring the rate. Similarly, the reverse reaction proceeds at a rate $K'.c.d.$, where c and d are the concentrations of the ester and water at the particular time. When the state of equilibrium is reached, we have:

$$K.a.b=K'.c.d.$$

Using one equivalent of acid and one equivalent of alcohol, Berthelot and St. Gilles showed that equilibrium is reached when 0·66 mol. of acid and of alcohol have been transformed, leaving 0·33 mol. in the free state; we thus have:

$$K\times0{\cdot}33\times0{\cdot}33=K'\times0{\cdot}66\times0{\cdot}66$$

$$\text{or } \frac{K}{K'}=\left[\frac{0{\cdot}66}{0{\cdot}33}\right]^2=4.$$

The ratio K/K' is denoted by K, and is usually termed the equilibrium constant. It is the

ratio of the constants for the direct and reverse reactions, and is independent of concentration, but may vary with temperature.

This equilibrium constant enables us to calculate the amount of acid transformed when any known quantities of the given acid and alcohol are mixed at the given temperature and kept until equilibrium is attained.

With a mixture of a, b, c, d equivalents of acid, alcohol, ester, and water at the given temperature, $a-x$ and $b-x$ equivalents of acid and alcohol will be present when equilibrium is attained, and $c+x$ and $d+x$ equivalents of ester and water will also be present, as each equivalent of acid reacts with an equivalent of alcohol and produces one equivalent of both ester and water.

$$\frac{K}{K'}=\frac{(c+x)(d+x)}{(a-x)(b-x)};\ \text{but}\ \frac{K}{K'}=4$$
$$\therefore \frac{(c+x)(d+x)}{(a-x)(b-x)}=4$$

and x can be calculated when a, b, c, d are known.

It is necessary to distinguish between esterification by means of the acid and alcohol alone, and esterification of an acid by an alcohol in the presence of a catalytic agent. The former process is generally termed 'direct esterification,' or sometimes 'autocatalytic esterification,' as it has been suggested that the organic acid itself can act as a catalyst to a certain extent. The second process is termed the catalytic method of esterification, and is the method most commonly used in the laboratory for the preparation of esters.

Catalytic esterification. The modern laboratory method is due to E. Fischer and Speier (Ber. 1895, 28, 3252). It consists in heating the acid with excess of alcohol, usually about five times the theoretical amount, in the presence of a catalyst. The most efficient catalysts are strong acids, and hydrogen chloride (about 3 p.c. of the alcohol) or concentrated sulphuric acid (about 10 p.c. of the alcohol) is generally used. When hydrogen chloride is used it is advisable to prepare a 3 p.c. solution of this in the alcohol before adding the organic acid. The 3 p.c. solution is best prepared by weighing the alcohol and passing in the dry gas by means of a delivery tube which just touches the surface of the liquid, and weighing from time to time until the requisite increase in weight is attained. The organic acid is then added, and the whole boiled in a reflux apparatus for 3 hours. The greater part of the alcohol is distilled off, the residue poured into about 5 times its volume of cold water, and the solution neutralised with sodium carbonate. It is then extracted with ether, the ethereal solution dried and distilled, when a 90 p.c. yield of the ester can usually be obtained. Esters which are readily hydrolysed by water, or esters which are extremely soluble in water, can sometimes be isolated by subjecting the reaction mixture to distillation under reduced pressure. J. and M. Phelps (Amer. J. Sci. 1907, [iv.] 24, 194) advise heating the acid, *e.g.* succinic or benzoic, with about its own weight of 1 p.c. alcoholic hydrogen chloride, and a small amount of solid zinc chloride at 100°–110°, and afterwards passing in a current of alcohol (compare *ibid.* 1908, 26, 281).

The function of the catalyst is to accelerate the rate of esterification; many acids which react very slowly with alcohol alone, *e.g.* acetic acid at the ordinary temperature, can be transformed rapidly into esters in the presence of a small amount of catalyst. Hydrogen chloride is a more efficient agent than sulphuric acid, the ratio being three to one (Kailan, Monatsh. 1909, 30, 21); but sulphuric acid is frequently used, as it is more convenient to work with. Phelps (Amer. J. Sci. 1908, [iv.] 260, 290, 296) has examined the action of various acid sulphates, *e.g.* $NaHSO_4$, $KHSO_4$, piperidine and aniline hydrogen sulphates, but finds that they are not so efficient as sulphuric acid, and similarly he has studied the action of metallic chlorides on the catalytic action of hydrogen chloride. Charcoal (Freundlich, Zeitsch. physikal. Chem. 1906, 57, 412) and finely divided platinum (Sudborough and Turner) also act as feeble catalysts. It is usually stated that the presence of the catalyst does not affect the equilibrium, and that provided the ratio of alcohol is kept the same, the percentage of ester formed when equilibrium has been obtained, is the same in both catalytic and direct processes; but Phelps does not agree with this statement.

The amount of ester formed by the catalytic process depends upon the specific acid and alcohol used, and tends to become less when the ester is readily hydrolysable. In the case of esters extremely soluble in water, or very readily hydrolysed, it is not advisable to pour into water, but to distil immediately under reduced pressure. Phelps and Eddy (Am. J. Sci. 1908, 26, 253) recommend adding solid potassium carbonate to the reaction mixture and distilling under reduced pressure.

Relationship between constitution and esterification using the catalytic method. V. Meyer and Sudborough (Ber. 1894, 27, 510, 1580, 3146) were the first to point out any clear relationship between the constitution of an acid and its conversion into an ester by the catalytic method. Their original method was to saturate the alcoholic solution of the acid with hydrogen chloride, to leave at the ordinary temperature for several hours, and then to isolate and weigh the ester formed. Subsequently the Fischer-Speier method was used. They were able to show that practically any substituted benzoic acid, in which the two ortho- positions with respect to the carboxylic group are substituted, does not yield appreciable amounts of ester when its alcoholic solution is saturated with hydrogen chloride and kept for several hours at the ordinary temperature, or when the acid is boiled with a 4 p.c. solution of hydrogen chloride in alcohol. All substituents react in much the same manner, *e.g.* CH_3, Cl, Br, F, I, CO_2H, NO_2, &c., but the substituents F, OH, CH_3 have not so marked an effect as nitro-, carboxylic, and halide radicals; *e.g.* acids of the type

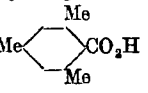
$$C_6H_2Me_3{\cdot}CO_2H(CO_2H:Me_3=1:2:4:6)$$

are esterified to an appreciable extent when hydrogen chloride is passed through their boiling alcoholic solutions for several hours (Meyer and Sudborough, Ber. 1894, 27, 1580; Meyer, *ibid.* 1895, 28, 182, 1254; compare also Kahn, *ibid.* 1902, 35, 3857).

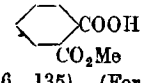
The presence of a second benzene nucleus, as in naphthalene- and anthracene-carboxylic acids,

has much the same effect as nitro- or halogen substituents; thus 2-chloro-1-naphthoic acid, anthracene-7-carboxylic acid and 1-chloroanthracene-9-carboxylic acid do not yield esters by the catalytic method, whereas the isomeric 3-chloro-2-naphthoic acid, anthracene-1-carboxylic acid, and 3-chloroanthracene-2-carboxylic acid yield 90 p.c. of ester under the same conditions.

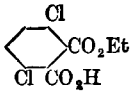
It has been shown by V. Meyer (Ber. 1895, 28, 3197; and Rupp, *ibid.* 1896, 29, 1625) that the dibasic acids:—tetrachloro-, tetrabromo-, and tetraiodo-terephthalic acids, tetrachloro-, tetrabromo-, and tetraiodo-*iso*phthalic acids, *i.e.* acids in which both carboxylic groups are diortho- substituted, do not yield esters when heated with a 3 p.c. solution of hydrogen chloride in alcohol. An acid in which one of the carboxylic groups is diortho- substituted and the other is not, yields an acid ester under similar conditions, *e.g.* 2:6-dimethylterephthalic acid $C_6H_2Me_2(CO_2H)_2$ gives



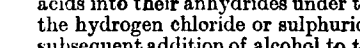
(Jannash and Weiler, Ber. 1895, 28, 531). Similarly, hemipinic acid, 3:4-dimethoxyphthalic acid, gives the acid ester



(Wegscheider, Monatsh. 1895, 16, 135). (For further examples, *see* Wegscheider, *ibid.* 1900, 21, 621, 638; 1902, 23, 405; McKenzie, Chem. Soc. Trans. 1901, 79, 1135.) An apparent exception is met with in the case of 3:6-dichlorophthalic acid, which, according to Graebe (Ber. 1900, 33, 2026), yields the acid ester



when its alcoholic solution is saturated with hydrogen chloride and kept at the ordinary temperature. Tetrachloro-, tetrabromo-, and tetraiodo-phthalic acids also yield acid esters (Rupp, *ibid.* 1896, 29, 1625); *o*-nitrophthalic acid and papaverinic acid (Miller, Annalen, 1881, 208, 243; Wegscheider and Lipschitz, Monatsh. 1900, 21, 790; Wegscheider, *ibid.* 1902, 23, 369) behave in a similar manner, yielding neutral esters, and it is probable that the esters are formed by the conversion of the acids into their anhydrides under the influence of the hydrogen chloride or sulphuric acid, and the subsequent addition of alcohol to the anhydrides. 3:6-Dichlorobenzoylbenzoic acid and tetrachlorobenzoylbenzoic acid are also readily esterified, and it is possible that these react with alcohol as the tautomeric hydroxyphthalides; *e.g.*:



(Graebe). The results obtained with tri- or even hexa-carboxylic acids show the same inhibiting effect of ortho- substituents. Thus trimesic acid, benzene 1:3:5-tricarboxylic acid, yields a neutral ester; hemimellitic acid, the 1:2:3-tricarboxylic acid, yields a dimethyl ester; pyromellitic acid, benzene-1:2:4:5-tetracarboxylic acid, yields a normal ester; prehnitic acid, 1:2:3:4-tetracarboxylic acid, gives a dimethyl ester in the cold, and the neutral ester on heating; the formation of the latter is probably due to the fact that an anhydride is first formed, and this, with methyl alcohol, gives the dimethyl ester

which is further esterified to the normal ester. Dinitro-pyromellitic acid, mellitic acid, and hexahydromellitic acid do not yield esters (Meyer, Ber. 1894, 27, 1590; 28, 182; 1896, 29, 840). *Iso*hydromellitic acid, on the other hand, yields a monomethyl ester (Van Loon, *ibid.* 1895, 28, 1272).

Substituted benzoic acids in which the substituents are not in ortho- positions, give good yields of esters by the Fischer-Speier method, and this difference in behaviour has been used for the following purposes: 1. Separation of an ortho-disubstituted benzoic acid from isomerides (compare Martz, Ber. 27, 3147, for separation of dinitro-benzoic acids; Jannash and Weiler, *ibid.* 3445, for separation of isomeric trimethyl-benzoic acids). Rosanoff and Prager (J. Amer. Chem. Soc. 1908, 30, 1912) show that a mixture of benzoic acid with an ortho- substituted benzoic acid can be separated by partial esterification in the cold with a 3 p.c. solution of hydrogen chloride in ethyl alcohol. 2. Determination of the constitution of particular substituted benzoic acids. (Compare V. Meyer, Ber. 1895, 28, 187, for 2-methyl-5-bromobenzoic acid; Zincke and Francke, Annalen, 1896, 293, 123, for 4-acetyl-5-bromo-*iso*-phthalic acid; and Matthews, Chem. Soc. Proc. 1900, 16, 187, for 2:3:5-trichlorobenzoic acid. *See* also Blaise, Compt. rend. 1898, 126, 733, for substituted succinic acids.)

When the carboxylic group is not directly attached to the benzene nucleus, but is united to a side chain, the presence of ortho- substituents does not prevent the formation of esters, *e.g.* 2:4:6-tribromo-3-aminophenylpropionic acid and 2:4:6-tribromophenylpropionic acid, mesitylacetic and mesitylglyoxylic acid all gave good yields of esters when the alcoholic solutions are saturated with hydrogen chloride. Kellas (Zeitsch. physikal. Chem. 1897, 24, 221) and Goldschmidt (Zeitsch. elect. Chem. 1909, 15, 4) have shown that the introduction of one ortho- substituent into the benzoic acid molecule retards esterification to an appreciable extent, the nitro- group having a greater inhibiting effect than Me, Cl, Br, or I. Kailan also shows that *o*-aminobenzoic acid hydrochloride is esterified more slowly than its isomerides (Monatsh. 1906, 27, 1038); but he finds that *o*-nitrocinnamic acid is esterified more readily than the *p*- and *m*-nitro acids (*ibid.* 1907, 28, 1163). Goldschmidt was able to show that using a dilute alcoholic solution of the acid with hydrogen chloride as catalyst, the velocity of the reaction can be determined by means of the equation for a unimolecular reaction, $K = 1/t(\log a/a-x)$; since under these conditions the mass of the alcohol can be regarded as constant, and the reaction is practically non-reversible in the presence of the large excess of alcohol. The concentration of the acid at any given moment can be determined by direct titration with standard barium hydroxide solution, using phenolphthalein as indicator. When, however,

the ester formed is readily hydrolysed, as in the case of ethyl formate, ethyl trichloracetate, and ethyl pyruvate, it is necessary to titrate with ammonium hydroxide solution, using litmus as indicator, as the end point is not definite when baryta is used, owing to the instantaneous hydrolysis of the ester by the baryta. The constant K is directly proportional to the concentration of the hydrogen chloride in the absence of water, and falls somewhat as t (time) increases, owing to the fact that the water produced during the esterification has a retarding effect. The influence of small amounts of water has been studied by Kailan (Monatsh. 1906, 27, 543, 997; 1907, 28, 115, 571, 673, 705, 965, 1069, 1137, 1187; 1908, 29, 799; 1909, 30, 1), who has shown that the relationship between the rate of esterification and the amount of water can be represented by means of an equation of the type, *e.g.* in the case of cinnamic acid

$$\frac{1}{K}=0{\cdot}665+\frac{4876}{c}-\frac{1{\cdot}678}{c^2}+\left(2{\cdot}911-\frac{3{\cdot}212}{c}+\frac{4{\cdot}358}{c^2}\right)w$$
$$+\left(-27{\cdot}54+\frac{31{\cdot}78}{c}-\frac{2{\cdot}284}{c^2}\right)w^2$$

for concentrations of water $w = 0{\cdot}3$ to $1{\cdot}3$, and for concentrations of hydrogen chloride $c = 0{\cdot}15$ to $0{\cdot}66$. (Compare also Fitzgerald and Lapworth, Chem. Soc. Trans. 1908, 93, 2168.)

Sirks (Rec. trav. chim. 1908, 27, 237) has obtained the following values for the esterification constants of the isomeric dinitrobenzoic acids at 25°, using ethyl alcohol containing a little water with hydrogen chloride as catalyst: 3:4-dinitro-acid, 0·0086; 3:5-acid, 0·0050; 2:3-acid, 0·0005; 2:5-acid, 0·0003; 2:4-acid, 0·0002; and 2:6-acid, nil. The values for $E^{25°}_{EtOH}$ obtained for benzoic, *m*-, and *o*-nitrobenzoic acids were 0·0132, 0·0071, 0·001[1].

These numbers indicate the retarding effect of one or two nitro-groups in the ortho-position; even one *m*-group retards, but the introduction of a second nitro-group into the meta-position of the *m*-nitro acid molecule, increases the rate.

From a comparison of the rates of esterification of these acids with their dissociation constants, Sirks comes to the conclusion that acids with small dissociation constants are esterified more readily by the catalytic method than acids with high dissociation constants; but an examination of certain alkyl-derivatives of aliphatic acids shows that the statement does not hold good generally.

Sudborough and Lloyd, by using Goldschmidt's method of determining esterification constants, have shown that the introduction of one substituent into the acetic acid molecule has a retarding effect, whatever the nature of the substituent. The introduction of two substituents usually has a more marked effect than one, and three a greater influence than two, when the two or three substituents are alike. A comparison of the esterification constants for the normal fatty acids gave the following values for $E^{15°}_{MeOH}$: formic, 1124, acetic 104, propionic 92, and from butyric to stearic values between 50 and 54. The introduction of a carbonyl-group in place of the α-methylene group of a normal fatty acid produces a retardation (Kailan, Monatsh. 1907, 28, 1137; Sudborough). The introduction of methyl- groups into the molecule of methyl hydrogen succinate also produces a lowering of the esterification constant (Bone, Sudborough, and Sprankling, Chem. Soc. Trans. 1904, 85, 534).

In the case of unsaturated acids, the following generalisations have been drawn (compare Sudborough and Lloyd, Chem. Soc. Trans. 1898, 73, 81; Sudborough and Roberts, *ibid.* 1905, 87, 1840; Sudborough and Thomas, *ibid.* 1907, 91, 1033; Sudborough and Gittins, *ibid.* 1909, 95, 315; Sudborough and Davies, *ibid.* 975). 1. An $\alpha\beta$-unsaturated acid is esterified much less readily than its saturated analogue; in many cases the ratio is 1:40. 2. An $\alpha\beta$-unsaturated acid is esterified far less readily than the isomeric acids, in which the double linking is further removed from the carboxyl-group. As a rule, $\beta\gamma$-unsaturated acids are esterified more readily than their saturated analogues; *e.g.* $\beta\gamma$-phenylcrotonic acid has $E^{15°}_{MeOH}$ 86·6, and the saturated γ-phenyl-*n*-butyric acid $E^{15°}_{MeOH}$ 56·25. $\gamma\delta$-Acids and other unsaturated acids, in which the double linking is further removed from the carboxyl-group, are esterified at much the same rate as the corresponding saturated acids; *e.g.* E for oleic acid is 54·3, and for palmitic acid 49·7. 3. In most cases the introduction of a substituent into the α-position in the acrylic acid molecule has a greater inhibiting effect than when introduced into the β-position. 4. The effect of a substituent in the cis-position is more marked than in the trans-, thus an acid of the

type $\begin{matrix} X-C-H \\ \| \\ Y-C-CO_2H \end{matrix}$ is more readily esterified

than the isomeride $\begin{matrix} H-C-X \\ \| \\ Y-C-CO_2H \end{matrix}$.

The difference in the rates of esterification of an $\alpha\beta$-unsaturated acid and the saturated analogue, a difference which has been confirmed by Kailan (Monatsh. 1907, 28, 1137) in the case of cinnamic and hydrocinnamic acids, affords a very convenient method for separating mixtures of the two. This is well shown in the preparation of hydrocinnamic acid. The acid is obtained by the reduction of cinnamic acid, and is liable to contain small amounts of the latter, which are difficult to remove by crystallisation, but a complete separation can be effected by the action of a dilute solution of hydrogen chloride in ethyl alcohol. The saturated acid is completely transformed into ester, and, under suitable conditions, the unsaturated acid remains unesterified. A similar method can also be used with advantage for the separation of a mixture of an $\alpha\beta$-unsaturated acid and the isomeric $\beta\gamma$-acid; this method is preferable to the older method used by Fittig, in which the $\beta\gamma$-acid was transformed into the γ-lactone (Sudborough and Thomas).

Gyr (Ber. 1908, 41, 4308) has determined the esterification constants of a number of mono-, di-, and tri-substituted acetic acids, and confirms the results obtained by Sudborough and Lloyd.

[1] The letter E is used to denote the esterification constant of an acid, using normal hydrogen chloride as catalyst, and the temperature and specific alcohol are also given, as the constant varies with these.

The values, for example, for acetic, phenyl acetic, diphenyl acetic, and triphenyl acetic, at 25° are respectively 7·76, 3·57, 0·20, and 0·001. Gyr worked with absolute methyl alcohol, and recommends boiling some three or four times with small amounts of metallic calcium in order to remove the last traces of water.

Kistiakowsky (Zeitsch. physikal. Chem. 1898, 27, 250) has determined the velocity of reaction of an acid and alcohol in mixtures of the alcohol and water containing hydrogen chloride. In this case the esterification and hydrolysis proceed side by side, and the velocity constants for the two are denoted by K and K'. Then:

$$K=\frac{1}{t}\cdot\frac{\xi}{a}\log_e\frac{\xi}{\xi-x} \text{ and } K'=\frac{1}{t}\cdot\frac{a-\xi}{a}\log_e\frac{\xi}{\xi-x}$$

$$K+K'=\frac{1}{t}\log_e\frac{\xi}{\xi-x},$$

when the amounts of water and alcohol are large compared with the amount of acid present. ξ denotes the gram-molecules of acid transformed into ester at equilibrium, and x the number of gram-molecules transformed at end of time t.

K can also be calculated from $K+K'$ by means of equation:

$$K=(K+K')\frac{\xi}{a}$$

The values of K and K' and also the value $\frac{\xi}{a}$ are independent of the original concentration of the organic acid.

The same values for K and K' are obtained when a mixture of acid, alcohol, water, and catalyst, or ester, alcohol, water, and catalyst are used, provided the proportion of water and alcohol and the concentration of the catalyst are kept the same.

The temperature coefficient between $t=25°$ and $t=30°$ is about 10 p.c. per degree, using mixtures of alcohol and water containing 13–70 p.c. alcohol.

The values of both K and K' fall on passing from formic to acetic, and again from acetic to monochloracetic.

The effect of the proportion of alcohol and water present is marked. The value of K in the case of formic acid rises from 0 to 300 as the percentage of alcohol increases from 0 to 91·4, whereas the value for K' falls from 198 to 60, as the percentage of alcohol is increased from 0 to 91·4. In the absence of a catalyst, the velocity of esterification falls as the organic acid is used up, whereas the velocity of hydrolysis is first small, and gradually increases as fresh acid is formed, and both K and K' diminish with an increase in the amount of alcohol present.

Direct method of esterification. Menschutkin, working with the fatty acids (J. pr. Chem. 1881, [ii.] 24, 49; *ibid.* 1882, [ii.] 25, 193; Ber. 1897, 30, 2783), was one of the first to draw attention to the relationship between the rate of esterification and the constitution of the acid and of the alcohol, and found that the amount of acid converted into ester in a given time diminished with the complexity of the acid molecule, and also with the complexity of the alcohol molecule. By heating a given amount of acetic acid with equivalent amounts of different alcohols for one hour at 135°, Menschutkin was able to show that, on the whole, a primary alcohol is esterified more rapidly than a secondary, and a secondary than a tertiary. Some of the results obtained by Menschutkin for primary alcohols are not true measures of velocity, as equilibrium had already been obtained within the hour. It is also pointed out that the introduction of side chains or of negative substituents into a primary alcohol also tends to lower the rate of esterification, and the greater the number of such groups introduced the more pronounced is the effect. The introduction of an olefine linking into the molecule of the alcohol in the $\alpha\beta$- position also diminishes the rate of esterification. Subsequent experiments made by heating the alcohol with given weights of acetic anhydride gave similar results. Still later work with hydroxy-polymethylenes (Chem. Soc. Trans. 1906, 89, 1533), using the acetic anhydride method, indicates that these compounds are esterified more readily than analogous open-chain compounds, *e.g.* the value for methyl-propyl-carbinol and cyclopentanol are respectively 98 and 189, and that cyclic tertiary alcohols are esterified least readily and primary most readily. The results also indicate that methyl- groups in the *o*- position with respect to the hydroxyl- group also produce retardation, but not to the same extent as when attached to the carbon atom to which the OH is attached. Michael and Wohlgast (Ber. 1909, 42, 3157) have determined the rates of esterification of trichloracetic acid with various alcohols at 25° and 50°, and give the following numbers, using the equation for a bimolecular reaction:—

Primary alcohols	$K\times10^5$ 25°	$K\times10^5$ 50°	Secondary	$K\times10^5$ 25°	Tertiary	$K\times10^5$ 25°
Methyl	3690	24,000	Dimethyl-carbinol	98	Ter-butyl	118
Ethyl	650	4,210	Methyl-ethyl „	90	Ter-amyl	248
Propyl	725		Methyl-propyl „	76		
Butyl	1200		Methyl-hexyl „	109		
*Iso*butyl	740					
Heptyl	1160					
Octyl	1860					
Cetyl	2590	16,300				

According to Michael, factors which are of importance are: 1. Degree of association of the alcohol; as this is greater in the case of the simpler alcohols, the rate of esterification would be reduced to a greater extent. 2. Readiness with which the alcohol decomposes into H and R·O· in order to react with the carbonyl- group. 3. The influence of alkyl- groups on the affinity of the R·O· and H for the unsaturated atoms of the carbonyl- group. Michael claims that his results do not afford the slightest evidence for the view that atoms or groups can produce effects by mere filling of space.

As regards the influence of the constitution of the acid on the velocity of esterification, Menschutkin drew the following conclusions as

the result of experiments made by heating the respective acids for one hour with *iso*butyl alcohol. The introduction of an alkyl- group into the formic acid molecule invariably produces a retardation in the esterification. The introduction of alkyl- groups into the acetic acid molecule also produces a retardation, and this is greatest when three alkyl- groups replace the three hydrogen, *e.g.* trimethylacetic acid, and is least when only one alkyl- group is introduced. Unsaturated acids of the type of crotonic and cinnamic are esterified less readily than their saturated analogues.

Lichty (Amer. Chem. J. 1895, 17, 27; 1896, 18, 590) found, however, that in the case of the chlorinated acetic acids the introduction of a chlorine atom into the acetic acid molecule tends to facilitate the formation of ester when the direct method is used. It is obvious that the results obtained by the direct and catalytic methods of esterification are not comparable, and Sudborough and Feilmann (Chem. Soc. Proc. 1897, 13, 241) have suggested that at least two factors are concerned in the process of esterification when using the same alcohol, viz. (1) strength of the acid esterified; (2) the presence of substituting groups in close proximity to the carboxyl- group. When the direct method of esterification is used, the former appears to be the determining factor, whereas with the catalytic method the latter is of primary importance; but in either case both factors are involved. Compare also Flürscheim, Chem. Soc. Trans. 1909, 95, 718.

Rosanoff and Prager (J. Amer. Chem. Soc. 1908, 30, 1895) have also shown that diortho-substituted benzoic acids can be esterified by the direct method, provided they are heated with excess of the alcohol at a comparatively high temperature (183°) for about 100 hours. The reaction proceeds even at the boiling-point of alcohol, but requires prolonged heating. Rosanoff and Prager determined both the velocity constant K and the reciprocal of the equilibrium constant, viz. $K'=K'/K$. They used different weights of alcohol and acid in each experiment, and by taking the volume of the solution into account, they calculated K by means of the equation:

$$K=\frac{2{\cdot}3026v}{t\sqrt{(a-b)^2+4abK'}}\times \log_{10}\frac{2ab-x(a+b-\sqrt{(a-b)^2+4abK'})}{2ab-x(a+b+\sqrt{(a-b)^2+4abK'})}$$

where a and b are the molar concentrations of the acid and alcohol, v is the volume of the mixture in litres, x the number of gram-molecules of the ester formed after time t (in days). The values of K obtained for a few acids are:

Benzoic		0·630
2 : 3 : 5-Tribromobenzoic		0·370
3 : 4 : 5-	„	0·900
2 : 4 : 6-	„	0·088
2 : 4 : 6-Trichlorobenzoic		0·031
Acetic		1·450
Propionic		0·950
*Iso*butyric		1·070
Trimethylacetic		0·180
Chloracetic		2·460
Dichloracetic		6·380 at 80°
Trichloracetic		12·000

and it is pointed out that in many of these cases an increase in velocity of esterification runs parallel with an increase in the electrolytic dissociation constants of the acids, although the two sets of constants are *not* proportional.

Michael and Oechslin (Ber. 1909, 42, 317) have determined the amounts of ester formed when various mono- substituted benzoic acids are heated with methyl alcohol in sealed tubes at 135° without a catalyst, but they did not determine the actual constants. They found that many *m*- and *p*- substituted benzoic acids containing negative substituents are esterified somewhat more readily than benzoic acid, but that an *ortho*- substituent, with the exception of Cl, tends to retard esterification, and that the effect is the greatest in the case of the methyl-group.

The following are some of the values obtained after 7 hours: benzoic 11·1, *o*-chlorobenzoic 11·9, *o*-bromobenzoic 10·4, *o*-iodobenzoic 9·7, *o*-nitrobenzoic 10·0, salicylic 7·7, and *o*-toluic 6·2.

The results obtained by Rosanoff and Prager and by Michael and Oeschelin are compatible with the view that at least two factors are concerned in esterification either by the catalytic or the direct method; that in the former case the chief factor is the presence of substituents in close proximity to the carboxyl- group (steric hindrance) whereas the strength of the acid, as measured by its dissociation constant, is of but secondary importance; in the direct method the relative values of the two factors are frequently the exact opposite. (Note: The dissociation constant for *s*-trichlorobenzoic acid is not known.) The results do not justify the conclusion drawn by both Rosanoff and Michael, that substituents do not retard esterification by mere space filling.

Other methods for preparing esters. Esters which cannot be obtained by direct esterification, *e.g.* the esters of diortho- substituted benzoic acids, can be prepared by the following methods: 1. Action of the alcohol on the acid chloride or acid anhydride. The latter action is accelerated by the presence of small amounts of a strong acid (Reychler, Bull. Soc. chim. Belg. 1907, 21, 428). 2. Action of the alkyl iodide on the dry silver salt. 3. Action of methyl sulphate on an aqueous solution of the sodium salt of the acid (Werner and Seybold, Ber. 1904, 37, 3658). 4. Action of an ethereal solution of diazomethane on the acid.

Sulphonic acids. Sulphonic acids do not give good yields of esters when warmed with alcohol alone or with alcohol and a mineral acid. This is probably due to the fact that the ester formed immediately reacts with the alcohol, giving the free acid and an ether:

$$C_6H_5{\cdot}SO_2{\cdot}OMe+MeOH=C_6H_5{\cdot}SO_2{\cdot}OH+Me_2O$$

(comp. Krafft and Roos, Ber. 1893, 26, 2823; Wegscheider and Furcht, Monatsh. 1902, 23, 1094). The esters are not formed when the sodium salt of the acid is warmed with alkyl iodide and alcohol (Wegscheider and Furcht); but can be obtained by the action of methyl sulphate on the acid or by the action of the alcohol on the acid chloride at low temperatures (Krafft, Ber. 1892, 25, 2256).

Esters of dibasic acids. A dibasic acid can give rise to both an acid and a normal ester,

e.g. $CO_2H{\cdot}CH_2{\cdot}CO_2H \rightarrow CO_2H{\cdot}CH_2{\cdot}CO_2Me$ and $CO_2Me{\cdot}CH_2{\cdot}CO_2Me$. With the exception of diortho- substituted aromatic dibasic acids, the normal esters can be obtained by the Fischer-Speier method of esterification. For the preparation of the acid esters, the following methods are resorted to: 1. Addition of alcohol or of sodium alkyl oxide to the acid anhydride. 2. Partial hydrolysis of the normal ester. 3. Partial esterification of the acid. 4. The action of alkyl iodides on the acid silver salts, if these can be prepared, or on the acid potassium salts. In the case of a symmetrical dibasic acid, the same acid ester is formed by all these methods, although, in most cases, except those coming under the first heading, the yields are not very good, as free acid and normal esters are also formed, and the separation is not always easy.

With an unsymmetrical dibasic acid, two isomeric acid esters (the *a* and the *b*) [1] can exist, and which of these is formed depends largely on which method of preparation is used. Wegscheider has carried out numerous experiments (comp. Monatsh. 1895, 16, 75; 1897, 18, 418, 629; 1899, 20, 685; 1900, 21, 621, 638, 787; 1902, 23, 317, 357, 369, 393, 405; 1903, 24, 413, 915; 1905, 26, 1039; 1906, 27, 487, 777; 1907, 28, 819; 1908, 29, 525, 531, 535, 541, 557; sulphonated benzoic acids, *ibid.* 1902, 23, 1093; tribasic acids, *ibid.* 1910, 31, 1253) on the following acids: hemipinic (3:4-dimethoxyphthalic), nitrohemipinic, camphoric, nitro-, bromo-, amino-, and hydroxy-terephthalic, 3- and 4-nitrophthalic, 4-hydroxyphthalic, phthalonic, homophthalic, aspartic, phenylsuccinic, and papaverinic, and has drawn the following conclusions under the assumption that the two carboxylic groups differ appreciably as regards their relative strength: 1. By the addition of alcohol to the anhydride and by the action of alkyl iodides on the acid potassium or acid silver salts, the stronger carboxyl- group is esterified, so that under these conditions *a*-acid esters are formed. If there is but little difference in the relative strengths of the two carboxyl-groups, then a mixture of the two acid esters is obtained, but the *a*-compound preponderates; *e.g.* $C_6H_2(CO_2H)_2(OMe)_2(1:2:3:4)$ gives, by these methods, the acid ester:

$$C_6H_2(CO_2H)(CO_2Et)(OMe)_2$$
$$1 \quad 2 \quad 3:4$$

$$CO_2H{\cdot}C_6H_3\begin{cases}CO\ (2)\\ O\ (3)\\ CO\end{cases}\ \text{(1)} \text{ gives } C_6H_3\begin{cases}CO_2H\ (1)\\ CO_2Me\ (2)\\ CO_2H\ (3)\end{cases}$$

Exception: phenyl succinic anhydride. Diazomethane and the acid give mainly neutral ester, but also small amounts of acid ester derived from the stronger carboxyl- group. 2. By the process of catalytic esterification the carboxylic acid group, which is freer from adjacent substituents, is esterified first, thus opianic acid gives the *b*- ester $C_6H_2(CO_2Et)(CO_2H)(OMe)_2$,
$$1 \quad 2 \quad 3:4$$
but neutral ester and small amounts of the *a*-isomeride may also be formed, especially if the conditions are such that anhydride formation can occur. The same rule holds good for direct esterification if the possibility of anhydride formation is excluded. 3. The addition of sodium alkylate in the absence of alcohol and water to the anhydride yields the *b*- acid ester, with appreciable amounts of the isomeride. 4. The partial hydrolysis of the neutral ester gives the acid ester, which is difficult to prepare by the method of catalytic esterification; *e.g.* dimethylhemipinate gives the *a*-acid ester. Exceptions: the hydrolysis of methyl hydroxyterephthalate, 4-hydroxyphthalate, 4-nitrophthalate, aminoterephthalate, phthalonate.

[1] The term *b*- ester is given to the acid ester with the higher dissociation constant, and the isomeride is termed the *a*- (Ber. 1902, 35, 4329; 1903, 36, 304).

Theories of esterification.—*Direct method:* The reaction between the acid and alcohol is not a simple ionic reaction, since the acid with the highest dissociation constant is not necessarily esterified most readily, and in the case of a dibasic acid it is not always the stronger CO_2H group which is esterified first. The view usually accepted at the present time is that an additive compound of alcohol and acid of the type

$$R{\cdot}C\begin{cases}OEt\\ OEt\\ OH\end{cases}$$

i.e. a dialkyl- derivative of an ortho-carboxylic acid, is first formed by the addition of a molecule of alcohol to the carbonyl- group of the acid (Wegscheider, Monatsh. 1895, 16, 137; Henry, Ber. 1877, 10, 2041). Michael suggests that before this additive compound is formed an unstable 'Kekulé double molecule' is formed, perhaps by the coming into play of the two latent valencies of the oxygen atoms:

$$R\begin{cases}C=O\begin{cases}OH\\ Et\end{cases}\\ OH\end{cases}$$

It is well known that many esters can form additive compounds with sodium ethoxide, and, therefore, presumably with ethyl alcohol, although compounds of the latter type have not been isolated. Pechmann (Ber. 1898, 31, 503) has been able to show that the esters of diortho-substituted benzoic acids cannot yield additive compounds with sodium ethoxide, probably owing to the space filling (steric hindrance) of the group in the ortho- position; by analogy, the diortho- substituted acids would not yield the orthocarboxylic acid derivative at all readily, and this would account for the fact that diortho-substituted benzoic acids are not readily esterified.

Catalytic esterification. According to Michael, the processes of direct and catalytic esterification are essentially different; the former is a reaction between the organic acid and alcohol, and the latter a reaction between the organic acid and an additive compound of the alcohol and catalyst (Ber. 1909, 42, 312). This reaction does not consist of addition to the carbonyl-group of the acid, but in union of the acid with the alcohol-catalyst complex to form a large 'double molecule,' which decomposes immediately into ester, water, and catalyst. The fact that esterification is facilitated by the presence of the catalyst is accounted for by the assumption that the alcohol-catalyst complex contains a greater store of energy, is therefore more reactive than the alcohol itself, and can more quickly develop the maximum entropy of the alcohol-acid system. It is questionable whether these views are in harmony with the facts established by Wegscheider, viz. that the same acid ester is obtained from an unsymmetrical dibasic acid, whether the direct or catalytic method of esterification is adopted, provided that anhydride formation is excluded. Goldschmidt also

comes to the conclusion that the two processes are essentially different (Zeitsch. Elektrochem. 1909, 15, 4). He claims to have shown that the presence of sodium trichloracetate does not depress the velocity of esterification of trichloracetic acid by the direct method, and, therefore, the direct esterification cannot be a simple case of hydrion catalysis. Later experiments of Sudborough and Turner show that the presence of salts of trichloracetic acid does diminish the rate of esterification of the acid, and hence Goldschmidt's conclusion is not justified. The fact that in direct esterification the strength of the acid is an important factor is compatible with the view that the organic acid itself plays the same part in direct esterification that the catalyst does in catalytic esterification. This view agrees again with the fact that the reaction in certain cases of direct esterification is bimolecular (Goldschmidt, Ber. 1896, 29, 2208), provided the reaction is not between the ions of acid and alcohol.

Kailan (Monatsh. 1908, 29, 799) is also of opinion that the processes of direct and catalytic esterification are not analogous, since the addition of a small amount of water increases the rate of esterification of trichloracetic acid by the direct method, but diminishes the activity of trichloracetic acid when it is used as a catalyst.

Various views are held with regard to the function of the catalyst. Goldschmidt and Uddy (Zeitsch. physikal. Chem. 1907, 60, 728; comp. also Ber. 1906, 39, 711, and Zeitsch. physikal. Chem. 1910, 70, 627) conclude that the hydrions of the catalyst are the active agents, since the activity of different acids is in the order of their relative strengths, *e.g.* the relative values of the acids hydrochloric, picric, trichloracetic, and dichloracetic as catalysts are indicated in the order given, and the addition of salts of the acid used as catalyst diminishes the activity of the catalyst. They further conclude that the hydrions unite with the alcohol, and that the complex ion $(C_2H_6O,H)^+$ is the active agent. They suggest the following modified formula for calculating the velocity constant:—

$$K.c=\frac{1}{t}(n+r+a)\log.\frac{a}{a-x}-x$$

where c = concentration of catalyst, n = concentration of water, and r = hydrolytic constant of the complex alcohol ion for

$$(C_2H_6O,H)^+ \quad r=1{\cdot}5.$$

The constants obtained by means of this equation agree better, and do not show the tendency to decrease as t increases, a tendency which is marked when the constants calculated by means of the ordinary equation for a unimolecular reaction are used.

A marked exception to the depressing effects of the addition of salts is met with in the case of hydrogen chloride, where the addition of chlorides such as calcium chloride, tetramethyl-ammonium chloride, and aniline hydrochloride, have no appreciable effect on the catalytic activity of hydrogen chloride (Goldschmidt; Sudborough).

Many chemists are of opinion that in catalytic esterification, as in catalytic hydrolysis of esters by means of mineral acids (*see* art. on HYDROLYSIS), a complex is formed between the substance transformed (acid in esterification and ester in hydrolysis) and the catalyst. This compound is probably an oxonium salt containing quadravalent oxygen, *e.g.* $R{\cdot}C(OH)(O{<}\overset{H}{Cl})$. The salt, only small amounts of which may be present, is ionised into $(R{\cdot}CO_2H,H)^+$ and Cl^-, and the esterification proceeds by the reaction of the complex cation with the alcohol (Acree and Johnson, Amer. Chem. J. 1907, 38, 334); *e.g.*:

$$(R{\cdot}CO_2H,H)^+ + C_2H_5OH = R{\cdot}CO_2Et + H_2O + H^+$$

and not with the ions of the alcohol as suggested by Lapworth. This reaction is more rapid than the simple reaction between the acid and alcohol, and in this way the accelerating effect of the catalyst is accounted for.

The retarding effects produced by small amounts of water are, according to Lapworth (Chem. Soc. Trans. 1908, 93, 2167, 2196), due to the water competing with the organic acid for the catalyst, *i.e.* acting as a feeble base, and giving rise to the complex ion $(H_2O,H)^+$, which is not catalytically active. The fact that in alcohol containing water, the velocity of esterification at constant volume decreases more rapidly than the concentration of the catalyst (Goldschmidt and Uddy, Zeitsch. physikal. Chem. 1907, 60, 735; Kailan, Monatsh. 1906, 27, 543, 997; Annalen, 1907, 351, 186), is also held to be opposed to the view that a complex hydrion is formed with the alcohol.

(For the conversion of acid amides into esters, and for the transformation of methyl into ethyl esters, both processes of alcoholysis, *see* art. HYDROLYSIS.) J. J. S.

ESTORAL *v.* SYNTHETIC DRUGS.

ESTRAMADURITE *v.* FERTILISERS.

ETHAL *v.* WAXES.

ETHYL

C_2H_5 or $CH_2{-}CH_2$

is a univalent basylous radicle not known in the free state, the body C_4H_{10} or $(C_2H_5)_2$ which was named ethyl (afterwards diethyl) by its discoverer, Frankland (Chem. Soc. Trans. 2, 263), being now regarded as butane.

Ethyl acetamide *v. Ethylamine.*

Ethyl acetate *v.* ACETIC ACID.

Ethyl alcohol *v.* ALCOHOL.

Ethyl antimonite $(C_2H_5O)_3Sb$; b.p. 115°–120°; from action of C_2H_5OH upon Sb_2O_3 in presence of anhydrous $CuSO_4$; colourless liquid (McKey, Chem. Soc. Trans. 1909, 95, 604).

Ethyl arsenite $(C_2H_5O)_3As$. A liquid formed by action of C_2H_5OH upon As_4O_6 in presence of anhydrous $CuSO_4$, the yield being 4·5 p.c. (Lang, McKey, and Gortner, Chem. Soc. Trans. 1908, 93, 1368). According to Crafts (Bull. Soc. chim. 1870, ii. 14, 99), it is obtained in very small yields by

(1) Action of Et_3SiO_3 upon As_4O_6 at 200°;

(2) Action of Ag_3AsO_3 upon EtI at 150°;

(3) Action of $AsBr_3$ upon NaOEt.

Auger (Compt. rend. 1906, 143, 907) obtained a yield of 1·2 p.c. by heating EtOH and As_4O_6 in a sealed tube far above the boiling-point of the alcohol.

Ethyl arsenate. A liquid boiling above 200° with partial decomposition. Decomposed by water immediately. Formed by heating together in sealed tubes at 100° Ag_3AsO_4 and EtI (Crafts, Bull. Soc. chim. 1870, ii. 14, 99).

Ethyl boride $(C_2H_5)_3B$. *Triethyl boride, Borethyl*; b.p. 95°; sp.gr. 0·696 at 23°; V.D. at 132° = 3·598; at 101·6° = 3·76; calc. = 3·399. From action of $Zn(C_2H_5)_2$ upon $(C_2H_5)_3BO_3$, or from BCl_3 and $Zn(C_2H_5)_2$ (Frankland, Trans. Roy. Soc. 1862, 167; Proc. Roy. Soc. 1876, 25, 165).

A spontaneously inflammable, colourless liquid burning with green flame; decomposed by HCl, evolving C_2H_6, and forming $B(C_2H_5)_2Cl$. Is slowly decomposed by water, and destroyed by HNO_3, with formation of boric acid. Absorbs NH_3, forming an oily liquid $NH_3B(C_2H_5)_3$ of an aromatic odour, which is fairly stable even in contact with O. $B(C_2H_5)_3$ absorbs O and forms $B(C_2H_5)_3O_2$; b.p. 125°. This, by the action of water, yields **ethylboric acid** $B(C_2H_5)(OH)_2$, a crystalline solid resembling naphthalene in appearance; can be sublimed at 40°; has a sweet taste, and acid action, but does not combine with bases. By action of $Zn(C_2H_5)_2$ upon this body we get $B(C_2H_5)(OC_2H_5)_2$ and $B(OC_2H_5)_3$; b.p. 112°; V.D. (dissoc.) 2·78. By further action of $Zn(C_2H_5)_2$ upon ethylboric acid we get $B(C_2H_5)_2OC_2H_5$; b.p. 102°; V.D. = 3·914. Water converts this into $B(C_2H_5)_2OH$, a spontaneously inflammable liquid, which absorbs oxygen, yielding $B(C_2H_5O)C_2H_5{\cdot}OH$; m.p. 8°.

Ethyl bromide C_2H_5Br. *Hydrobromic* or *Bromhydric ether*; m.p. −116·0° (Ladenburg and Krugel, Ber. 32, 1818) −125·5° (Schneider, Zeitsch. physikal. Chem. 22, 233); b.p. 38·37° (Regnault, J. 1863, 70); b.p. 40·7° at 57 mm. (Pierre); sp.gr. 1·4189 at 15° (Mendeléeff), 1·4733 at 0° (Pierre), 1·4685 at 13·5°; crit. temp. 236° (Pawlewski, Ber. 16, 2633).

Preparation.—1. By action of P and Br upon alcohol (Serullas, Ann. Chim. Phys. [2] 34, 99). 40 parts red P and 160 parts absolute alcohol are slowly mixed with 100 parts Br, kept cool until all action is over; the mixture is then distilled, and the distillate purified by washing with water and rectification (Personne, Compt. rend. 52, 468).—2. Absolute alcohol is heated with Br and distilled, and the distillate is freed from excess of Br by washing with KOH and redistillation (Löwig, Annalen, 3, 288).—3. 4 parts KBr and 5 parts of a mixture of 2 parts H_2SO_4 and 1 part alcohol of 96 p.c. are distilled, and distillate purified as above (De Vrij, J. 1857, 441).—4. C_2H_4 in presence of $AlBr_3$ at 0° combines with HBr to form C_2H_5Br (Gustavson, J. Russ. Phys. Chem. Soc. 16, 95). To prepare pure C_2H_5Br, the commercially pure bromide is shaken with H_2SO_4 and allowed to separate. It is then shaken with dilute alkali and distilled with 10 p.c. of sweet almond oil (Adrian, Chem. Zentr. 1895, i. 20).

Ethyl bromide is a colourless liquid with a sweet taste, and burning after-taste. Its vapour has anæsthetic properties (Robin, Compt. rend. 34, 649; Webster, Bio. Chem. J. 1906, i. 328; Cole, J. Physiol. 29). It is slightly soluble in water, and miscible with alcohol and ether. The vapour is decomposed by heat, yielding C_2H_4 and HBr, or, if the temperature be higher, C is deposited (Löwig). Burns in air with a green flame, evolving HBr. By introduction of Cl two isomeric bodies of the composition C_2H_4ClBr, b.p. 84·5° and 104°–108°, and 2 isomerides of composition $C_2H_3Cl_2Br$, b.p. 137°, 151° (Lescœur, Bull. Soc. chim. 1878, 29, 483) are obtained. At 100° Br reacts, forming $CH_2Br{\cdot}CH_2Br$, whilst at 200° $CH_3{\cdot}CHBr_2$ is the product (Meyer and Müller, Ber. 24, 4247; J. pr. chem. [2] 46, 161). By action of Br and P upon alcohol, we get, further, $C_2H_4Br_2$, b.p. 160°; $C_2H_3Br_3$, b.p. 180°; $C_2H_2Br_4$, b.p. 196°–200° (Bertrand, Finot, Bull. Soc. chim. 34, 28) (*v. Ethylene bromide*). Heated with $AlBr_3$, yields successively $C_2H_4Br_2$, $C_2H_2Br_4$, and C_2Br_6 (Mouneyrat, Compt. rend. 127, 109). With ammonia it yields $NH_2(C_2H_5)$,HBr; and with ethylamine, diethylammonium bromide $NH(C_2H_5)_2$,HBr; similarly, with diethylamine, it yields $N(C_2H_5)_3HBr$.

Ethyl chloride C_2H_5Cl. *Chlorhydric* or *Hydrochloric ether*: m.p. −142·5° (Schneider, Zeitsch. physikal. Chem. 22, 233); b.p. 12·5° (Regnault, J. 1863, 67); sp.gr. 0·9214 at 0°; 0·9176 at 8°, 0·920 at 0° (Pierre), 0·851 at b.p. (Ramsay, Chem. Soc. Trans. 35, 470); S.V. 75·8 (Kopp). (Roubiquet and Colin, Ann. Chim. Phys. [2] 1, 343; Regnault, *ibid.* 71, 355; Kühlman, Annalen, 33, 108; Löwig, Pogg. Ann. 14, 346; Gm. 7, 367; Gerh. 11, 308).

From alcohol by the action of S_2Cl_2 or metallic chlorides (Rouelle [1759]); from alcohol and HCl (Basse [1801]). Composition first ascertained by Robiquet and Colin. Also formed by action of Cl upon C_2H_6 (Darling, Annalen, 150, 216), and of HCl upon ether in sealed tubes (Berthelot).

The action of HCl upon alcohol gives a very poor yield of C_2H_5Cl, unless $ZnCl_2$ is added to the alcohol before passing in HCl (Groves, Chem. Soc. Trans. 1874, 636). Krüger (J. pr. Chem. [2] 14, 193) recommends that a mixture of 1 part of $ZnCl_2$ in 82 parts of alcohol should be saturated with HCl gas in the cold, and then heated to boiling, HCl being passed in during distillation. A reflux condenser stops the alcohol vapour, and the C_2H_5Cl passes on and is collected in a well-cooled receiver.

The formation of C_2H_5Cl in this process is partly due to the action of HCl upon alcohol; and partly to the union of the nascent C_2H_4 with HCl (Schorlemmer, Chem. Soc. Trans. 1875, 308); this view is sustained by the fact that if amyl alcohol be thus treated, both primary and secondary amyl alcohol are produced, and the latter can only be formed from the radicle C_5H_{10}. Ethyl chloride is also formed by the action of PCl_5 upon alcohol, and also, to some extent, by the action of Cl upon alcohol. Hence the formation of ethyl chloride in the manufacture of chloral.

It is a colourless mobile liquid; has a pungent ethereal smell, and a sweetish taste, and burns with a green-edged flame, evolving HCl. It is sparingly soluble in water, but mixes readily with alcohol and ether. It dissolves phosphorus, sulphur, fats, oils, and many resins. It combines with many metallic chlorides—*e.g.* $SbCl_5$, Fe_2Cl_6—to form crystalline compounds.

It is used in medicine like ether, but, on account of its volatility, it is mixed with an equal volume of alcohol, and is then known as 'alcoholised muriatic ether, B.P.' It is decomposed at a red heat into C_2H_4 and HCl; at higher temperatures carbon separates, and CH_4, H, and HCl are set free. Strong HNO_3, when boiling, liberates HCl and forms $C_2H_5NO_3$ in

small quantity (Thenard, Boullay). SO_3 absorbs it, forming $SO_3{\cdot}C_2H_5Cl$, a fuming liquid, b.p. 130° —probably the three isomerides $C_2H_5O{\cdot}SO_2{\cdot}Cl$, $CH_2{\cdot}ClCH_2{\cdot}SO_2{\cdot}OH$, and $CH_2(OH){\cdot}CH_2SO_2{\cdot}Cl$ (Purgold, Zeitsch. Chem. 1868, 669; Ber. 6, 502). When vapour of C_2H_5Cl is passed through boiling H_2SO_4, HCl is evolved (Thénard), also C_2H_4 and SO_2 (Boullay). When the vapour is led through a tube containing heated soda-lime, a mixture of CH_4 and H is evolved, and $NaC_2H_3O_2$ and Na_2CO_3 are formed (L. Meyer, Annalen, 139, 282), while, according to Dumas and Stas, C_2H_4 and NaCl are formed. On $AgNO_3$,C_2H_5Cl has no action until after prolonged contact, but even after some months only a very small quantity of AgCl is formed (Thénard, Boullay); but AgCl is rapidly thrown down when C_2H_5Cl is heated with a solution of $AgNO_3$ in sealed tubes (G. C. Foster).

Heated with bromine and iron wire at 100°, C_2H_5Br and ethylene dibromide are formed (V. Meyer and Petrenko-Kritschenko, Ber. 25, 3307).

NH_3 has only a slight action at ordinary temperatures, but on heating a mixture of NH_3 and C_2H_5Cl, ethylene and a deposit of NH_4Cl are formed (Dumas and Stas, Ann. Chim. Phys. 73, 154). When a mixture of ethereal NH_3 and C_2H_5Cl is exposed to sunlight, crystals of ethylamine hydrochloride separate (Stas). When heated with alcoholic NH_3 to 100° in sealed tubes, $NH_2(C_2H_5)$,HCl is also produced, together with traces of $NH(C_2H_5)_2$,HCl and $N(C_2H_5)_3$,C_2H_5Cl (Groves, Chem. Soc. Trans. 1861, 13, 331). KOH slowly removes Cl from C_2H_5Cl, yielding (in aqueous sol.) alcohol and KCl. Alcoholic KOH and C_2H_5Cl heated to 100° in sealed tube deposits KCl and forms $(C_2H_5)_2O$ (Balard, Ann. Chim. Phys. [3] 12, 302). Passed into heated sol. of K_2S, ethyl sulphide is formed; with alcoholic KHS, mercaptan is formed (Regnault).

Chlorine in the sunlight yields di-, tri-, tetra-, penta-, and hexa- chloro- derivatives of ethane (Regnault); of the dichloro- derivatives $CH_3{\cdot}CHCl_2$ is the main product. If, however, ethyl chloride is heated with a halogen carrier, $CH_2Cl{\cdot}CH_2Cl$ is the chief product (D'Ahns and Kautzsch, J. pr. Chem. [2] 1909, 80, 305; Staedel *ibid.* 303; Ber. 6, 1403; Meyer and Muller, J. pr. Chem. [2] 46, 161).

Trichlorethane $C_2H_3Cl_3$.

1. *Chlorethylene chloride* $CH_2Cl{\cdot}CHCl_2$; b.p. 115° (Pierre, Annalen, 80, 127), 113·7° at 760 mm. (Städel, Ber. 15, 2563), 113·5°–114° at 753·2 (Schiff, Annalen, 220·97); sp.gr. 1·4223 at 0° (P.), 1·4577 at 9·4°/4°, 1·2945 at 113·5°/4° (Schiff), 1·4406 at 25·6°; μ_A = 1·4719 at 22° Rx = 42·26 (Kanonnikow), from C_2H_3Cl (Regnault, Ann. Chim. Phys. [2] 69, 151), or $CHCl_2.CH_3$ (Meyer and Müller, J. pr. Chem. [2] 46, 174), and $SbCl_5$.

2. *Ethenyl trichloride* $CH_3{\cdot}CCl_3$; b.p. 74·5° (Geuther, J. 1870, 435); 74·1° at 760 mm. (Städel, Ber. 15, 2563); sp.gr. 1·3465 at 0° (Pierre, Annalen, 80, 127), 1·372 at 16° (Regnault, Annalen, 33, 317), 1·3657 at 0°, 1·3249 at 26°; μ_A = 1·4199 at 21°; Rx = 42·0 (Kanonnikow); by the chlorination of ethyl chloride (Regnault, *ibid.* 33, 317). Decomposed by sodium ethoxide, giving $C_2H_2Cl{\cdot}O{\cdot}C_2H_5$, $C_2H_4O_2$, and $C_2H_3(OEt)_3$.

Tetrachlorethane $C_2H_2Cl_4$.

1. *as*-$CH_2Cl{\cdot}CCl_3$; b.p. 135° (Regnault, Ann. Chim. Phys. [2] 69, 162), 138·6° (Pierre, Annalen, 80, 130), 135·1° (corr.) (Geuther, Brockhoff, J. 1873, 317); sp.gr. 1·6116 at 0° (P.), 1·576 at 19° (R.), 1·5825 at 0°, 1·5424 at 26°; μ_A at $t°$ = 1·4772−0·000437t; Rx = 50·72 (Kanonnikow). Formed by chlorination of ethyl chloride (Laurent, Annalen, 22, 292); or action of Cl upon $CH_2Cl{\cdot}CHCl_2$ (Regnault); by heating at 110° acetylene tetrachloride and $AlCl_3$ (Mouneyrat, Bull. Soc. chim. 1898, 19, 499). Decomposed by sodium ethoxide into $C_2HCl_2{\cdot}O{\cdot}C_2H_5$ and $CH_2(OC_2H_5)CO_2Na$.

2. *s*-$CHCl_2{\cdot}CHCl_2$; b.p. 147·2°; sp.gr. 4°/4° = 1·6208, 17°/17° = 1·6013; μ_D at 17° = 1·495587±0·000006 (Veley, Proc. Roy. Soc. 1910, B 82, 217); Rx = 50·6 (Kanonnikow) From C_2H_2 and $SbCl_5$ (Berthelot, Jungfleisch, Annalen, Suppl. 7, 254), from dichloraldehyde and PCl_5 (Paternò, Pisati); from ethylene chloride and $AlCl_3$ at 75° if Cl and C_2H_2 be led into the mixture (Mouneyrat); by long heating yields HCl and C_6Cl_6.

If S_2Cl_2 and 1 p.c. of its weight of reduced iron be saturated with Cl, and if the excess Cl be removed with CO_2, and then dry acetylene be passed in at a temperature of 40°, and the cycle repeated until no more C_2H_2 is absorbed, *sym*-tetrachloroethane, pentachloroethane, and hexachloroethane are produced, the two latter in small quantity (Michel, Zeitsch. angew. Chem. 1906, 19, 1095). The *sym*-tetrachlorethane is distilled off from the mixture, either alone or in steam (D. R. P. 174068; Chem. Soc. Abstr. 1906, i. 169).

Pentachlorethane $CHCl_2{\cdot}CCl_3$; b.p. 159·1° (corr.); 161·7° at 760 mm. (Städel); m.p. —18°; sp.gr. 1·7089 at 0°, 1·6926 at 10·15°/4° (Thorpe, Chem. Soc. Trans. 37, 192); μ_A = 1·4871 at 25·1°; R_∞ = 59·05 (Kanonnikow). By action of chlorine upon C_2H_5Cl also from chloral and PCl_3 (Paternò, Annalen, 151, 117), or $AlCl_3$ (Mouneyrat, Bull. Soc. chim. 1898, 19, 260).

Hexachlorethane $CCl_3{\cdot}CCl_3$ (*v. Carbon trichloride*, art. CARBON).

(For mixed halogen derivatives of ethane, *see* Mouneyrat, Bull. Soc. chim. 1898, 19, 499; Swartz, Rec. trav. chim. 17, 234 and 235; Bull. Acad. Roy Belg. 36, 519; *ibid.* 1909, 60 and 728; *ibid.* 1899, ii. 281; Elbs and Newmann, J. pr. Chem. 1898, 58, 245; Biltz, Ber. 1902, 35, 3524; Lemoult, Compt. rend. 1903, 136, 1333; Besson, Bull. Soc. chim. [3] 11, 920; Nef, Annalen, 298, 353, 354, 358, and 360; Thiele and Peter, *ibid.* 369, 149; Lawrie, Amer. Chem. J. 1906, 36, 487.)

Ethyl *iso*cyanate. *Ethyl carbimide*, $C_2H_5N:C:O$; b.p. 60°; sp.gr. 0·8981; heat of formation (Lemoult, Compt. rend. 1898, 126, 43); absorption spectrum (Hartley, Dobbie and Walker, Chem. Soc. Trans. 1901, 856). By the action of dry KCNO upon $KC_2H_5SO_4$ at 180°–250° (Wurtz, Ann. Chim. Phys. 1854 [3] 42, 43); distillate is a mixture of *iso*cyanate and *iso*cyanurate, which can easily be separated by distillation. By passing CNBr into absolute alcohol and ether (Ponomarew, Ber. 1882, 15, 515; Mulder, Rec. trav. chim. 1, 210; 2, 133); by passing CNBr (Mulder, *ibid.* 3, 306) or CNCl (Cloëz, Compt. rend. 44, 428; Annalen, 102,

355) into C_2H_5ONa in absolute alcohol; by the action of diazomethane on *sym*-ethylnitrourea (Degner and Pechmann, Ber. 1897, 30, 653); by heating the mercuric chloride derivative of ethyl thiolcarbamate (Anschütz, Annalen, 1908, 359, 202).

In 1895 Nef (*ibid.* 287, 310) showed that the compound hitherto known as ethyl cyanate was ethyl *iso*cyanate. Ethyl *iso*cyanate is a mobile liquid having a suffocating smell. It is decomposed by water into diethylcarbamide, and by ammonia into ethylcarbamide.

Ethyl cyanide, Propionitrile $C_2H_5{\cdot}C{:}N$, m.p. −103·5° (Schneider, Zeitsch. physikal. Chem. 22, 233); b.p. 98·1° (corr.) (Engler, Annalen, 133, 153); 97·08° (corr.) (Thorpe, Chem. Soc. Trans. 37, 205); sp.gr. 0·8010 at 0°, 0·7938 at 7·36°/4° (Thorpe), 0·7015 at 97°/4° (Schiff, Ber. 19, 567); H. C. 446·7 Cals. (Berthelot and Petit, Compt. rend. 108, 1217); latent heat of vapourisation (Louguinine, Chem. Zentr. 1900, i. 451); molecular refraction 25·10 (Brühl, Zeitsch. physikal. Chem. 16, 214; Eykman, Rec. trav. chim. 12, 172; Costa, J. 1891, 336); magnetic rotation (Perkin, Chem. Soc. Trans. 55, 701); crit. temp. 291·2°; crit. density 0·2401 (Ter-Gazarian, J. Chim. Phys. 1906, 4, 140).

From $Ba(C_2H_5SO_4)_2$ and KCN (Pelouze, Annalen, 10, 249), from cyanogen chloride and $Zn(C_2H_5)_2$ (Gal, Zeitsch. Chem. 1868, 252), from $Zn(C_2H_5)_2$ and $(CN)_2$ (Frankland and Graham, Chem. Soc. Trans. 37, 740), from propionamide and P_2O_5 (Dumas, Malaguti and Leblanc, Annalen, 74, 329). By heating ethyl *iso*cyanide to 240° (Nef, *ibid.* 280, 296).

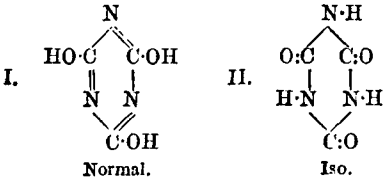
Preparation.—By heating C_2H_5I with pure KCN and alcohol to 180°; C_2H_5Cl dissolved in three times its weight of alcohol is heated with KCN to 100° or 150° (Rossi, Annalen, 159, 79). C_2H_5I is heated with KCN in closed tubes to 180°, and the product distilled, and the distillate is freed from excess of C_2H_5I by means of a solution of $CaCl_2$, upon which the C_2H_5CN swims, while the heavier C_2H_5I sinks to the bottom (Williamson, Phil. Mag. [4] 2, 205; Gauthier, Ann. Chim. Phys. [4] 17, 180).

It is a mobile colourless liquid with an agreeable odour, soluble in water, from which $CaCl_2$ or NaCl causes it to separate; miscibility with water (Rothmund, Zeitsch. physikal. Chem. 26, 453); V.D. 1·928. It combines with the hydracids, *e.g.* HCl; the product C_2H_5NHCl forms monoclinic prisms soluble in water and melting at 121° (Gauthier). HCl gas passed into a well-cooled solution of the cyanide in acetic acid gives acetyl chloride and $C_2H_5CONH_2{\cdot}HCl$ (Colson, Bull. Soc. chim. [3] 17, 57). Chlorine combines with C_2H_5N to form dichlorpropionitrile $CH_3{\cdot}CCl_2{\cdot}CN$, a liquid body, b.p. 103°–107° which polymerises on standing to a solid $(C_2H_3Cl_2N)_2$. Propionitrile also forms compounds with metallic chlorides and with cyanogen chloride. $C_2H_5N{\cdot}CNCl$ is a liquid decomposed by water; b.p. 60°–68° (Henecke, Annalen, 106, 280). Compounds with $AlCl_3$ (*v.* Perrier, Compt. rend. 1895, 120, 1423). Propionitrile is hydrolysed by acids or alkalis yielding propionic acid; electrolytic reduction yields *n*-propylamine (Ahrens, Zeitsch. Elektrochem. 1896, 3, 99). By the action of metallic sodium, polymerisation ensues, the products being sodium cyanide, ethane, and α-iminopropionylethyl cyanide (Meyer, J. pr. Chem. [2] 38, 326; 45, 63).

Ethyl *iso*cyanide, *Ethyl carbylamine* $C_2H_5N:C$; b.p. 79°; sp.gr. 0·759 at 4°, 0·7150 at 44·5° (Gauthier, Ann. Chim. Phys. [4] 17, 233); molecular refraction 16·26 (Costa, Gazz. chim. ital. 22, i. 104). By the interaction of C_2H_5I and AgCN (Gauthier, Annalen, 151, 239); by distilling KCN with $KC_2H_5SO_4$, propionitrile also being formed; by digesting ethylamine with chloroform and alcoholic potash (Hofmann, *ibid.* 147, 107).

It is a colourless liquid having a very repulsive smell. It is transformed into propionitrile by heating at 240°; by heating with alcoholic H_2S, ethylthioformamide is produced; with sulphur and CS_2 ethylthiocarbimide; combines with CNCl; with C_2H_5Cl at −10° yields $C_2H_5N(Cl)O{\cdot}C_2H_5$ (Nef, *ibid.* 280, 296). HgO oxidises it to $C_2H_5N:C:O$. Yields a chloride $C_2H_5N:CCl_2$, by treatment with SO_2Cl in ether at −15°; an oil, b.p. 102° (Nef, *l.c.*). Yields a bromide, $C_2H_5N:CBr_2$, with bromine in $CHCl_3$. This gives ethylamine dibromide with water, ethyl *iso*cyanide dibromide hydrobromide and ethylthiocarbimide with H_2S, ethyl *iso*cyanide dibromide hydrochloride with dry HCl, an oily ethiodide with ethyl iodide, and diphenylethylguanidine with aniline (Guillimand, Bull. Soc. chim. 1904, iii. 31, 605; 1905, iii. 33, 652). Compounds with cobaltous, ferrous, and ferric chlorides (*v.* Hofmann and Bugge, Ber. 1907, 40, 3759). (For further reactions, *v.* Nef, *l.c.*)

Ethyl derivatives of cyanuric acid. Although cyanuric acid exists in only one modification, probably the *iso*-(II.) esters derived from the tautomeric forms (I. and II.) are known.



Ethyl cyanurate $(C_2H_5OCN)_3$; m.p. 29°, b.p. 275° (Claësson, J. pr. Chem. [2] 33, 131). By action of CNCl on C_2H_5ONa (Hofmann, Ber. 19, 2061); also from C_2H_5ONa (3 mols.) and trimethyl cyanurate (H); from CNI or CNBr and C_2H_5I (Ponomarew, Bull. Soc. chim. [ii.] 41, 315); by heating the lead salt of the diethyl ester (P.); together with ethyl *iso*cyanurate by treating silver cyanurate with C_2H_5I (C., P.); from di-potassium cyanurate and C_2H_5I(P.).

Oily liquid readily soluble in alcohol, ether, $CHCl_3$ and CS_2, sparingly so in water. Converted into ethyl *iso*cyanurate by long heating at 180°–200°; yields cyanuric acid with HCl, cyanuric chloride with PCl_5, melamine with strong ammonia and the diethyl ester with baryta water.

Diethyl cyanurate, Diethylcyanuric acid $HO(CN)_3(C_2H_5O)_2$ (Ponomarew, Ber. 18, 3267; Hofmann, *ibid.* 19, 2077). By warming ethyl cyanurate with concentrated baryta water; by treating methyl cyanurate or mono-potassium cyanurate with C_2H_5I.

Thick plates from water, insoluble in ether, sparingly soluble in alcohol. Decomposes on heating into diethyl *iso*cyanurate; yields cyanuric acid on warming with HCl. Pb salt and C_2H_5I yield triethyl cyanurate, but if C_2H_5I contains free I, triethyl *iso*cyanurate also formed.

Ethyl isocyanurate, Triethylcarbimide $(C_2H_5NCO)_3$; m.p. 95°; b.p. 276°; absorption spectrum (Hartley, Dobbie and Walker, Chem. Soc. Trans. 1901, 849); heat of formation (Lemoult, Compt. rend. 125, 869). By polymerisation of C_2H_5NCO(H. D. and W.); also from potassium cyanate or cyanurate, or from Pb salt of the diethyl ester and KC_2H_5SO; by heating ethyl cyanurate at 180°-200°; together with ethyl cyanurate from silver cyanurate and C_2H_5I (Habich and Limpricht, Annalen, 109, 102).

Rhombic prisms (Rammelsberg, J. 1857, 273; Fock, Ber. 19, 2076) moderately soluble in hot water, readily so in alcohol. KOH yields $N(C_2H_5)H_2$ and K_2CO_3.

Diethyl isocyanurate, Diethylcyanuric acid $H(NCO)_3(C_2H_5)_2$, m.p. 173°. Obtained in preparing the triethyl ester (Habich and Limpricht, *l.c.*); together with cyanuric acid by heating anhydrous mono-potassium cyanurate with C_2H_5I at 170°-180° (Ponomarew, Ber. 18, 3270); by heating diethyl cyanurate (Hofmann, *ibid.* 19, 2078).

Hexagonal columns, readily soluble in hot water, alcohol, and ether, sparingly so in cold water. Yields CO_2 and $N(C_2H_5)H_2$ by heating in a sealed tube at 100°. Pb salt and C_2H_5I yield ethyl *iso*cyanurate.

Ethyl ferrocyanide $(C_2H_5)_4Fe(CN)_6$. From $Ag_4Fe(CN)_6$ and C_2H_5I (Freund, Ber. 21, 935). Rhombic crystals from $CHCl_3$, easily soluble in water and alcohol, insoluble in ether, ligroin, and CS_2. Decomposed at 212°-214°, with formation of ethyl *iso*cyanide. The aqueous solution gives a deep violet tint with $FeCl_3$, and a white precipitate with $HgCl_2$. Molecular weight by cryoscopic method indicates the monomolecular formula (Buchbock, Zeitsch. physikal. Chem. 23, 157).

Ethyl fluoride C_2H_5F. Obtained impure by action of CaF and H_2SO_4 upon C_2H_5OH (Reinsch, J. pr. Chem. 1840, 19, 314); by heating $KC_2H_5S_4$ and KF·HF (Fremy, Compt. rend. 1854, 38, 393). Prepared pure from AgF and C_2H_5I Moissan, Ann. Chim. Phys. 1890, [6] 19, 272). Colourless gas with ethereal odour, liquefying at −32° under atmospheric pressure. Burns in air with a blue flame. Readily soluble in C_2H_5Br, C_2H_5I, C_2H_5OH, and ether. Decomposed at 100° by heating with KOH in a sealed tube into KF, C_2H_5OH, and ether.

Ethyl formamide $H{\cdot}CONHC_2H_5$; b.p. 199°; sp.gr. 0·952 at 21°. By distilling an aqueous solution of $H{\cdot}COONH_3(C_2H_5)$; separates from distillate upon addition of KOH (Linnemann). By action of $NH_2(C_2H_5)$ upon $CCl_3{\cdot}CHO$ (Hofmann, Ber. 5, 217); a thick colourless liquid.

Ethyl formate $H{\cdot}CO_2C_2H_5$; b.p. 54·4° at 760 mm., sp.gr. 0·9376 at 0°/4°; b.p. 53·4°-53·6° at 754·5 mm., sp.gr. 0·8731 at 53·4°/4° (R. Schiff, Annalen, 220, 106); b.p. at 760 mm. 54·3°, sp.gr. 0·9480 at 0°/4°; critical temperature, 235·3°; critical pressure, 35,550 mm. (Young and Thomas, Chem. Soc Trans. 1893, 1193). Capillarity constant at boiling-point, $a^2 = 4{\cdot}528$ (Schiff, Annalen, 223, 75); H.C. p. 388 cals. (Berthelot, Ogier) 391·7 (Delépine).

By distilling a mixture of 6 parts alcohol (90 p.c.), 7 parts sodium formate and 10 parts (conc.) H_2SO_4 (Liebig); by distilling a mixture of ethyl oxalate with oxalic acid (Löwig, J. 1861, 599); by heating a mixture of glycerol, oxalic acid, and alcohol in a reflux condenser, and then distilling (Lorin, Bull. Soc. chim. [ii.] 5, 12). On the large scale a mixture of 9 parts of starch and 29 parts of MnO_2 (of 85 p.c.) is heated with 28 parts of H_2SO_4, 5 parts H_2O, and 15 parts of alcohol (85 p.c.) (Stinde, Dingl. poly. J. 181, 402).

A mobile colourless liquid with a pleasant aromatic smell; is used for flavouring arrack and rum; is decomposed by water, for which it has strong affinity. Sodium in absolute ether decomposes it into CO,H and C_2H_5ONa (Freer and Sherman, Amer. Chem. J. 18, 581). Cl forms with it in sunlight *dichlorethyl formate* $H{\cdot}CO_2C_2H_3Cl_2$, a colourless oily liquid, decomposed on heating, and which by action of alkalis is decomposed into acetic, formic, and hydrochloric acids. By further action of Cl in sunlight, *perchlorethyl formate* $Cl{\cdot}CO_2C_2Cl_5$, b.p. 200°, sp.gr. 1·705 at 18°, is formed (Cloëz, Ann. Chim. Phys. [3] 17, 297).

Ethyl hydrate *v.* ALCOHOL.

Ethyl hydride, Ethane, *Dimethyl* C_2H_6 (Frankland and Kolbe, Chem. Soc. Trans. 1, 60); m.p. −171·4°; b.p. at 749 *mm.* −85·4° (Ladenburg and Krügel, Ber. 32, 1821). Gas; sp.gr. 1·036, condensed at 4° and 46 atmospheres pressure (Cailletet, J. 1877, 68); critical constants (*v* Hainlen, Annalen, 282, 245; Olszewski Ber. 1894, 27, 3306; and Keunen, Chem. Zentr. 1897, ii. 540); sol. in water at *t*°

$$(1)\ \frac{9{\cdot}4556-0{\cdot}35324t+0{\cdot}006278t^2}{100}$$

$$(2)\ \frac{8{\cdot}710-0{\cdot}33242t+0{\cdot}00603t^2}{100}$$

(1) Schickendantz (Annalen, 109, 116), (2) Bunsen (Gasometry). Sol. in alcohol = 1·5 (Berthelot, J. 1867, 344); H.C. p. 373·3 Cals. (Th.) = 372·3 (Berthelot, Ann. Chim. Phys. [6] 30, 559); H.F. (from amorphous C) = 11·7 Cals. (B.); occurs in crude petroleum.

Pittsburg gas consists of ethane mixed with a little CH_4 and CO_2, and is used for smelting and lighting purposes.

By action of K upon C_2H_5CN, also by action of water upon $Zn(C_2H_5)_2$ (Frankland and Kolbe, Chem. Soc. Trans. 3, 338); by action of Zn upon C_2H_5I in presence of water; by electrolysis of acetic acid or acetates (Kolbe, Annalen, 69, 279); by heating 9 parts of C_2H_5I with 2·6 parts of $AlCl_3$ to 140° or 150° (Köhnlein, Per. 16, 562); by action of $Hg(C_2H_5)_2$ upon H_2SO_4 (Schorlemmer, Annalen, 132, 234); by heating an excess of PaO_2 with acetic anhydride and sand (Schützenberger, Zeitsch. Chem. 1865, 703; Darling, Annalen, 150, 216); by the action of nascent H (from ZnCu couple or Zn dust) upon a mixture of C_2H_5I and C_2H_5OH (Sabanejeff, Ber. 9, 810). By reducing C_2H_4 or C_2H_2 with H in presence of reduced Ni (Sabatier and Senderens, Compt. rend. 124, 1360; 128, 1173). From EtI and potassium hydride in sealed tubes at 180°-200°

(Moissan, *ibid.* 134, 389). Reduced Ni at 325° breaks ethane up into C and CH_4 (Berthelot).

Ethyl iodide C_2H_5I (Gay-Lussac, Ann. Chim. Phys. [1] 91, 89; Serullas, *ibid.* [2] 25, 323 and 42, 119; Frankland, Chem. Soc. Trans. 2, 263; 3, 32); m.p. −118° (Schneider); b.p. 72·34° (Linnemann, Annalen, 160, 204), b.p. 71·3° (Andrews), 71·6° (Frankland), b.p. at 756 mm. 71·9°–72° (Linebarger); sp.gr. 1·9444 at 14·5° (L.), 1·9755 at 0° (Pierre), 1·9309 at 15° (Mendeléeff), sp.gr. 1·1810 at 72·2°/4° (Schiff), sp.gr. 1·9653 at 4°, 1·9433 at 15°, 1·9243 at 25° (Perkin); V.D. 5·417 (Marchand).

From alcohol and HI (Gay-Lussac); from alcohol, iodine, and phosphorus (Serullas). Personne (Compt. rend. 42, 468) suggested the use of red P, and, according to Beilstein (Annalen, 126, 250), 1 part red P and 5 parts of alcohol (90 p.c.) are placed in a retort, and 10 parts of iodine slowly added. After 24 hours the C_2H_5I is distilled off, washed with NaOH solution and with water, and dried over $CaCl_2$. Crismer (Ber. 1884, 649) dissolves I in liquid paraffin adds yellow P and then alcohol. Walker (Chem. Soc. Trans. 1892, 717; *cf. ibid.* 1905, 1596) obtains a 93 p.c. yield from alcohol, iodine, and equal parts of red and yellow phosphorus. Prepared in quantitative yield by adding Et_2SO_4 slowly to a warm concentrated aqueous solution of KI (Weinland and Schmid, D. R. P. 175209). Also from action of HI upon ether (Cottrel Rogers), and together with iodoform and NaI by electrolysis of a solution of 20 grams C_2H_5COONa, and 20 grams KI in 20 c.c. of water (Miller, Hofer, and Reindel).

C_2H_5I is a colourless, pleasantly smelling liquid, almost insoluble in water, but miscible with alcohol and ether. It precipitates silver from its solutions in the cold, easily forms double compounds with silver salts, metals, and ammonia. Br displaces the I, and forms C_2H_5Br; Cl forms C_2H_5Cl (Dumas, Stas, Annalen, 35, 162). ICl forms C_2H_5Cl and I_2. HCl has no action, but, on the contrary, C_2H_5Cl is decomposed by HI into C_2H_5I and HCl (Lieben, Zeitsch. Chem. 1868, 712). By action of HI at 150°, ethane and iodine are formed. HNO_3 also causes the separation of I (Marchand, J. pr. Chem. 1884, 33, 186). Metallic Ag abstracts I, and leaves butane (C_4H_{10}). By heating with water to 150°, we get alcohol (Reynoso, J. 1856, 567); with excess of alcohol yields ether and some C_2H_4 (Lieben, Rossi, Annalen, 158, 166). Is gradually turned brown by exposure to light, owing to formation of free I and liberation of butane (Frankland, Chem. Soc. Trans. 3, 322). In presence of mercury the reaction is much more rapid, owing to combination of the liberated I with Hg. Is used largely for the preparation of other ethyl compounds.

Ethyl nitrate $C_2H_5{\cdot}O{\cdot}NO_2$, *Nitric ether*; m.p. −112° (Schneider); b.p. 86·3° at 728·4 mm.; sp.gr. 1·1322 at 0°, 1·1123 at 15·5° (Kopp, Annalen, 98, 367); b.p. 87·6°; sp.gr. 1·1305 at 4°, 1·1159 at 15°, 1·1044 at 25° (Perkin); H.F.p. = 40,870; H.F.v. = 38,750; H.C. = 325, 690 (Th. 4, 214). Obtained from alcohol by the action of nitric acid in presence of some substance which will destroy nitrous acid, *e.g.* urea (Millon, Ann. Chim. Phys. [3] 8, 233).

Preparation.—400 grams of pure nitric acid sp.gr. 1·40, previously heated with 1 p.c. of urea in order to destroy lower oxides of nitrogen, are mixed with 300 grams absolute alcohol and 100 grams of urea nitrate, and distilled; when half the liquid has distilled off, a mixture of 400 grams of nitric acid and 300 grams of alcohol is allowed to drop into the retort and the distillation continued (Lossen, Annalen, Suppl. 6, 220).

Silver nitrate, heated with ethyl iodide (or bromide) and alcohol, yields, not ethyl nitrate, but the nitrite, together with aldehyde (Bertrand, Bull. Soc. chim. 33, [ii.] 566). If, however, EtI be added gradually to powdered $AgNO_3$, kept cool, a theoretical yield of $EtNO_3$ is formed (Von Biron, J. Russ. Phys. Chem. Soc. 30, 667).

Ethyl nitrate is a colourless liquid with pleasant odour and taste; almost insoluble in water, but miscible with alcohol and ether. Ammonia forms ethylamine nitrate; nascent hydrogen yields hydroxylamine and other bases (Lossen). Sulphuretted hydrogen yields mercaptan (Kopp, Annalen, 64, 320). Alcoholic potash decomposes it with separation of crystals of potassium nitrate.

Ethyl nitrite $C_2H_5{\cdot}O{\cdot}NO$, *Nitrous ether*; b.p. 16·4° (Liebig), 17° (Mohr, J. 1854, 561; Brown, Pharm. J. 15, 400), 17·5° (Dunstan and Dymond, *ibid.* 18, 861); sp.gr. 0·900 at 15·5° (Br.); 0·917 at 0°/0° (D. and D.); H.F.p. = 30,610; H.F.v. = 28,870 (Th. 4, 217).

This body was discovered in 1681 by Kunkel. Obtained from alcohol by action of nitric acid, especially in presence of some oxidisable matter, *e.g.* copper.

Preparation.—500 grams of potassium nitrite and 1 litre alcohol (45 p.c.) are mixed and cooled by means of ice; a mixture of sulphuric acid (500 grams), water (500 grams), and alcohol (500 grams) is then slowly dropped in, the heat produced volatilises the ether, which is condensed in an efficient condenser (Feldhaus, Annalen, 126, 71). Dunstan and Dymond (*l.c.*) recommend that 34·5 grams sodium nitrite in 120 grams water be slowly mixed with a mixture of 13·5 grams of sulphuric acid with 32 grams alcohol and about 75 c.c. water kept cool by ice. The ethyl nitrite separates out as a layer floating on the surface. As thus prepared, the liquid contains only trace of alcohol, from which it is freed by shaking with water. Alkali ethyl sulphates react with alkali nitrites, yielding nitrous ester and nitroethane (Ray and Neogi, Chem. Soc. Trans. 1906. 1900). Also formed by the interaction of $MgSO_4$, $NaNO_2$, and C_2H_5OH (Matuschek, Chem. Zeit. 1905, 29, 115).

Ethyl nitrite is a mobile liquid with a pleasant ethereal smell and taste, liable to undergo decomposition, especially in presence of water. It can be preserved if mixed with alcohol and a small quantity of glycerol. It is decomposed by sulphides in accordance with the following equation:

$$C_2H_5NO_2+3H_2S=NH_3+C_2H_6O+H_2O+3S$$

(Kopp, Annalen, 64, 321).

It is slightly soluble in water and miscible with alcohol. Mixed with alcohol it constitutes the 'sweet spirit of nitre,' *spiritus ætheris nitrosi*, of the British Pharmacopœia, which is thus prepared: 1 pint of rectified spirit is mixed with 2 fluid ozs. of sulphuric acid and 2½ ozs. of nitric acid. The mixture is run into a retort containing 2 ozs. of fine copper wire. 12 ozs. are distilled

off at 77°. ½ oz. more of nitric acid is then added, and 3 ozs. more are distilled off. The distillate is then mixed with 2 pints of rectified spirit.

Ethyl oxide $(C_2H_5)_2O$, **Ether**, *Ethyl ether, Vinic ether;* formerly called *Sulphuric ether, Phosphoric ether*, &c., according to the acid used in its preparation; m.p. −117·6° (Archibald and McIntosh), m.p. −112·6° (Ladenburg, and Krugel); b.p. 34·97° (Regnault), 34·6° at 762 mm. (Schiff, Annalen, 220, 332), 34·9° (Kopp); sp.gr. 0·7360 at 0°, 0·7185 at 17·5° (Hager), 0·6950 at 34·6°/4° (Schiff), 0·7024 at 15°, 0·7099 at 25°/25°, 0·7201 at 15°/15° (Perkin, Chem. Soc. Trans. 45, 474), sp.gr. 0·71982 at 15°/15° (Wade and Finnemore), sp.gr. 0·7183 at 17·1° (Brühl), sp.gr. 0·70942 at 25° (Linebarger); M.M. = 4·777 at 20°; freezes at −129° to a crystalline mass, which melts at −117·4° (Olzewski, Monatsh. 5, 128); capillarity constant at b.p. $a^2 = 4·521$ (Schiff); S. at 17·5° = 8; critical temperature, 194°; critical pressure, 35·61 atmospheres (Ramsay and Young). Vapour tension 67·49 mm. at −20°; 182·34 mm. at 0°; 286·4 mm. at 10°; 433·2 at 20°; 636·3 at 30°.

The preparation of ether from alcohol and sulphuric acid was first described by Valerius Cordus (1540), and the method of making this 'oleum vitrioli dulce' was published in 1552 by Conrad Gessner. Frobenius, 1730, named it sulphuric ether. Val. Rose (Scher. J. 4, 253) showed that it contained no sulphur, but its composition was first made out by Saussure and also by Dumas and Boullay (Ann. Chim. Phys. [2] 36, 294). Its constitution was first studied by Liebig (Annalen, 60, 31; 23, 39) and Regnault (Ann. Chim. Phys. [2] 71, 352). Williamson, in 1850-51 (B. A. 1850, 65, and Phil. Mag. [3] 37, 350), established the views now held as to its constitution and formation.

Formation.—From alcohol, by action of phosphoric or arsenic acid (Boullay); by action of boron fluoride (Desfosses, Ann. Chim. Phys. [2] 36, 294); of $ZnCl_2$ (Masson, Annalen, 31, 63); of $SnCl_4$, and other metallic chlorides (Kühlmann, *ibid.* 33, 97, 192). From alcohol by heating with dry NH_4Cl to 260°–400° (Berthelot, Annalen, 83, 110). From C_2H_5NaO and C_2H_5I (Williamson). From alcohol and HCl, HBr, or HI at 200° or 240°, or by heating alcohol with $ZnCl_2$, $SnCl_4$, $HgCl_2$, $CaCl_2$, $MgSO_4$, or chrome alum to 300° (Reynoso, Ann. Chim. Phys. [3] 48, 385). Also from C_2H_5Br or C_2H_5I and HgO (Reynoso), or from C_2H_5I and Na_2O (Green, Bull. Soc. chim. [ii.] 29, 458).

The continuous method now adopted is due to Boullay (J. Pharm. Chim. 1, 97), and the true explanation of the action was first given by Williamson (*l.c.*). The alcohol and sulphuric acid first form $C_2H_5HSO_4$ and H_2O, and then, by the action of $C_2H_5HSO_4$ upon more alcohol, $(C_2H_5)_2O$ and H_2SO_4 are formed. That this is true Williamson proved by using amyl sulphuric acid and ethyl alcohol, when amyl-ethyl ether was produced (*cf.* Prunier, J. Pharm. Chim. 1897, 5, 513). Addition of $Al_2(SO_4)_3$ increases rate of production of ether owing to catalytic action (Senderens, Compt. rend. 1910, 151, 392).

Preparation.—Boullay's method is usually employed. A mixture of 9 parts H_2SO_4 with 5 parts of alcohol (90 p.c.) is placed in a retort, and alcohol is slowly dropped in and the temperature is maintained between 130° and 140°. An iron retort lined with lead is usually employed, and the ordinary mercurial thermometer, which is, of course, liable to fracture, is replaced by a bulbed tube containing some non-drying oil. The tube is then either exhausted by the air-pump, and hermetically sealed, or its open end is closed by a plug of cotton wool, and two marks are made on the tube corresponding to positions of the surface of the oil at 130° and 140° respectively. In order to avoid risk of explosion by contact of the vapour with direct flame, coils of lead tubing, conveying superheated steam or the vapour of some liquid of high boiling-point (*e.g.* coal-tar phenol), are used as a source of heat. The distillate is treated with milk of lime or solution of soda in order to remove the SO_2 which is always simultaneously formed. It is then rectified in an apparatus devised by Mohr, which consists of a still from which the vapour is led through a vessel kept at 38° by warm water. Here the alcohol and water vapours are condensed, and the ether passes over, and is condensed in an efficient condenser.

By means of an apparatus devised by Soubeiran, ether can be prepared in a fairly pure state by one operation. A mixture of about 30 lbs. of H_2SO_4 with 20 lbs. of alcohol of 85 p.c. is heated rapidly to 130° in a copper still, to the bottom of which two tubes convey alcohol from a tinned copper reservoir. The neck of the retort (which is of lead) is connected with the first condenser, which is a copper vessel kept warm by allowing the waste water from the worm tub (where the ether is condensed) to flow over the outside of it. Here the steam and vapour of alcohol are condensed, and the liquid formed can be drawn off from below by means of a stopcock. The ether vapour then passes on to the purifier, which consists of a vessel filled with wood charcoal saturated with a solution of caustic soda, which not only removes the SO_2, but also absorbs the oil of wine. The pure ether passes on, and is condensed in a well-cooled worm. The greatest yield of ether is obtained at 140°–145°; below this temperature the yield is less, and above this much SO_2 is evolved (Prescott and Norton, Amer. Chem. J. 6, 243). Other apparatus have been described by Annaratone (Fr. Pat. 408089; J. Soc. Chem. Ind. 1910, 592) and Fritzsche (Zeitsch. anal. Chem. 1897, 36, 298). Sulphuric acid has been largely replaced by benzenesulphonic acid in this preparation (Krafft, Ber. 26, 2831; D. R. P. 69115; Frdl. iii. 11).

Commercial ether contains water, alcohol, aldehyde, and vinyl alcohol. The last may be removed by shaking with water or treatment with bromine, phenylhydrazine, or potassium hydroxide (Poleck and Thümmel, Ber. 22, 2863), and the other impurities by treatment with dry $Fe(OH)_2$, prepared from crystallised $FeSO_4$, and an equimolecular weight of powdered lime (Gaborini, Bull. Assoc. Chim. Sucr. Dist. 1909, 26, 1165); by treatment with potassium hydroxide and powdered potassium permanganate, and finally drying with calcium chloride (Fierz; Wade and Finnemore, Chem. Soc. Trans. 1909, 1842; Francois, Chem. Zentr. 1897, ii. 144; Fritsch, Chem. Zeit. 1909, 33, 759). Phosphorus pentoxide may be

substituted for calcium chloride (Lieben, Annalen, Suppl. 7, 218). (For other methods, *v.* Guigues, J. Pharm. Chim. 1906, 24, 204; and Ekenberg, Zeitsch. anal. Chem. 36, 245.)

Wade and Finnemore (*l.c.*) find that ether and water form a binary mixture, b.p. 34·15°, containing 1·3 p.c. water, and that slight traces of alcohol greatly increase the solubility of water in ether. 1 gram ether dissolves 0·023 gram water at 15°–20° and 0·019 at 10° (*cf.* Schunke, Zeitsch. physikal. Chem. 14, 331; Napier, Bull. Soc. chim. 29 [ii.] 129); 1 gram water absorbs at 0°, 0·12465; at 10°, 0·09599; at 20°, 0·07487; at 30°, 0·06370 gram ether (Schunke, *l.c.*; Tolloczko, Ber. 28, 808; Klobbie, Zeitsch. physikal. Chem. 24, 615; Osaka, J. Soc. Chem. Ind. 1909, 625). If ether be shaken with an equal volume of CS_2, a turbidity is produced if water be present.

Decompositions.—Pt black, CrO_3 or HNO_3 oxidise ether to acetic acid; ozone produces ethyl peroxide. Ether vapour and air at 100°, in the presence of a copper catalyser and platinum-black, yield acetaldehyde and formaldehyde (Orlow, J. Russ. Phys. Chem. Soc. 1908, 40, 799; *cf.* Legler, Annalen, 217, 382). When ozonised oxygen is passed into ether, a solution is obtained containing $C_2H_2O_4$, $C_2H_4O_2$, and H_2O_2, also a small quantity of CH_2O_2 (A. W. Wright). Ether combines with H_2SO_4 to form $C_2H_5HSO_4$; by action of SO_3 we first get $(C_2H_5)_2SO_4$, but by excess of SO_3, $C_2H_5HS_2O_7$, and a small quantity of a body of the composition $CH_2(SO_3C_2H_5)_2$ are formed. When ether is heated with water and a small quantity of H_2SO_4 to 150°–180°, alcohol is formed (Erlenmeyer, Zeitsch. Chem. 1868, 343). According to Lieben (Annalen, 165, 136), the reaction goes on, though very slowly, without H_2SO_4, and at the ordinary temperature. Ether combines easily with HI and yields C_2H_5I (Silva, Ber. 8, 903), and is decomposed by heating with zinc-dust into C_2H_4 and water (Jahn, Monatsh. 1, 675); bromine and aqueous ether yield bromacetaldehyde (Maugin, Compt. rend. 1908, 147, 747).

A hydrate $(C_2H_5)_2O,2H_2O$ is known; it is a solid body, which only exists below −3·5°, and is obtained by the rapid evaporation of aqueous ether on filter paper (Tanret, Bull. Soc. chim. 30, 505; Compt. rend. 87, 765). Dry ether and chlorine at −80° yield a white crystalline chloride $(C_2H_5)_2OCl_2$, m.p. −51°; bromine similarly yields a reddish-yellow bromide $(C_2H_5)_2OBr_2$, m.p. −40° (McIntosh, Chem. Soc. Trans. 1905, 789). A bromide $(C_2H_5)_2OBr_3$, red plates, m.p. 22°, is also known (Schutzenberger, Annalen, 167, 86).

Ether combines with various metallic salts and forms crystalline bodies, *e.g.* $BeCl_2$, $2(C_2H_5)_2O$, large prisms (Atterberg, Ber. 9, 856);

$$HgBr_2,3(C_2H_5)_2O$$

(Nickles, J. 1861, 200); $AlBr_3,(C_2H_5)_2O$ (N.). $TiCl_4,(C_2H_5)_2O$; crystalline; m.p. 42°–45°; b.p. 118°–120°, decomposes into $TiCl_3(OC_2H_5)$ (Bedson, Annalen, 180, 236; Chem. Soc. Trans. 1876, 1, 311).

Properties.—A colourless mobile liquid with pleasant smell. Volatilises very quickly, and by so doing produces great cold. It is extremely inflammable, and its vapour, which is very heavy, forms an explosive mixture with air. Ether is readily soluble in concentrated HCl solution (Draper, Chem. News, 35, 87), and in concentrated H_2SO_4, from which it is separated by addition of ice (Riedel, D. R. P. 52982, Frdl. ii. 551). It is miscible with almost all organic liquids, and with liquid CO_2. It is a good solvent for resins, fats, alkaloids, &c., and sulphur and phosphorus dissolve in it to a small extent. It also dissolves I and many salts, *e.g.* Fe_2Cl_6, $HgCl_2$, $PtCl_4$, and many gases, notably ammonia.

Its vapour when inhaled produces insensibility (Faraday, 1818), and it is used as an anæsthetic in surgery. It is also occasionally used in surgery for producing local anæsthesia; this is done by directing a spray of ether upon the skin, when the extreme cold produced by evaporation produces complete insensibility.

It is also used as a solvent in the preparation of collodion, in the extraction of tannic acids, of several alkaloids, &c.

Chlorine acts violently upon ether, setting fire to it, and liberating carbon (Cruikshank). If the ether be kept cool by ice, and in the dark, substitution products are obtained. The Cl replaces the H atom by atom from one ethyl group first, in the following order: $\overset{2}{C}H\overset{3}{H}\overset{4}{C}H\overset{1}{H}\overset{5}{O}C_2H_5$ (Lieben, Annalen, 111, 121; 146, 180; Abelganz, 164, 197; Jacobsen, Ber. 4, 215; also Liebig, Annalen, 1, 220; Malaguti, Ann. Chim. Phys. [2] 70, 338; [3] 16, 5; Fritsch and Schumacher, Annalen, 279, 302).

Monochlorether, *Monochlorethyl oxide*

$$CH_3{\cdot}CHCl{\cdot}O{\cdot}C_2H_5;$$

b.p. 97°–98°; by the chlorination of ether (Lieben); by saturating a mixture of aldehyde and alcohol with HCl (Frapolli, Wurtz, Annalen, 108, 226); by the action of PCl_5 upon acetal (Bachmann, *ibid.* 218, 39). It is decomposed by H_2SO_4 into HCl, C_2H_4O, and $C_2H_5{\cdot}OH$. C_2H_5ONa forms NaCl and acetal; water decomposes it into HCl, aldehyde, and alcohol (Laatsch, Annalen, 218, 36).

Dichlorether, *Dichlorethyl oxide*

$$CH_2Cl{\cdot}CHCl{\cdot}O{\cdot}C_2H_5;$$

b.p. 140°–145°; sp.gr. 1·174 at 23°; by action of Cl upon ether (Malaguti, Annalen, 32, 15); by action of HCl upon a mixture of chloraldehyde and $C_2H_5{\cdot}OH$ (Natterer, Monatsh. 5, 496); by action of HCl upon chloracetal (N.).

Dichlorether is decomposed on heating in a tube into C_2H_5Cl and other products. C_2H_5ONa forms first *chloracetal* $CH_2Cl{\cdot}CH(OC_2H_5)_2$. By heating with excess of C_2H_5ONa in sealed tubes, *ethyl glycol acetal* $CH_2(OC_2H_5)CH(OC_2H_5)_2$ is formed. In ethereal solution, $Zn(C_2H_5)_2$ yields *ethyl chlorether* $CH_2Cl{\cdot}CH(C_2H_5)OC_2H_5$; b.p. 141°; sp.gr. 0·9735 at 0°. With excess of $Zn(C_2H_5)_2$ we get $CH_2(C_2H_5)CH(C_2H_5)OC_2H_5$; b.p. 131·4° at 749·6 mm.; sp.gr. 0·7865 at 0° (Lieben, Annalen, 178, 14). Strong caustic potash forms alcohol, a body $C_4H_{16}Cl_2O_3$, a little glycollic acid, and two isomeric bodies of the composition $C_4H_9ClO_2$ (Albejanz, *ibid.* 164, 218): *α*-$C_4H_9ClO_2$, *chloraldehyde alcoholate* $CH_2Cl{\cdot}CH(OH)O{\cdot}C_2H_5$, b.p. 93°–95°; and *β*-$C_4H_9ClO_2$ *oxychlorether* $CH_2OH{\cdot}CHCl{\cdot}O{\cdot}C_2H_5$, also formed by chlorination of ether (Jacobsen, Ber. 4, 217), b.p. 151°–155°. With $NH_2{\cdot}OH$ yields glyoxime (Hantzsch and Wild, Annalen, 289, 293).

It is decomposed by water, and in presence of marble yields monochloracetaldehyde alcoholate, which, on distillation, gives monochloraldehyde and monochloracetal (Fritsch and Schumacher, *ibid.* 279, 301).

Trichlorether $CHCl_2 \cdot CHCl \cdot O \cdot C_2H_5$; b.p. 167°–168°, 155°–158° (Copaux), 170°–175° (Oddo and Mameli); sp.gr. 1·3303 at 14° (O. and M.), By the action of PCl_5 upon dichloracetal $CHCl_2 \cdot CH(OC_2H_5)_2$ (Krey, J. 1876, 475); by hydrolysis of the compound formed by action of chlorine on triethyl boric ester (Copaux, Compt. rend. 127, 721); by chlorinating $\alpha\beta$-dichloroethyl ether with 1 molecule of Cl at temperature of boiling saturated salt solution. At 230°–240° n a sealed tube, yields dichloroaldehyde and C_2H_5Cl. HCl at 110° for 6 hours, and distillation with concentrated H_2SO_4, yield the same products. Conversely, dichloroaldehyde in alcohol with HCl yields trichloroether. Boiled with water, trichloroether yields acetaldehyde, dichloroacetaldehyde hydrate (m.p. 55°–56°, b.p. 96·5°–97·5°), dichloroacetal, and other very complex compounds (Oddo and Mameli, Gazz. chim. ital. 33, ii. 373; also *ibid.* 36, i. 480); decomposed by heating with C_2H_5ONa, yielding *dichloracetal.*

Tetrachlorether $CCl_3 \cdot CHCl \cdot O \cdot C_2H_5$; b.p. 189·4° at 749·1 mm., 79° at 16 mm., 189·7° at 758·7 mm.; sp.gr. 1·4225 at 18°/4° (Weber and Foster, J. Amer. Chem. Soc. 31, 1410); sp. gr. 1·4379 at 0°, 1·4182 at 15·2°. Formed by action of Cl upon monochlorether in contact with I (Wurtz, Vogt, Zeitsch. Chem. 1871, 689), or of chloral alcoholate $CCl_3 \cdot CH(OH)O \cdot C_2H_5$ upon PCl_5 (Henry, Ber. 5, 101, 435; Paternò, Pisati, J. 1872, 303). From *trichlorvinyl ethyl ether* and chlorine (Godefroy). A liquid with a camphor-like smell, decomposed by heating with water into C_2H_5OH, HCl, and chloral. Alcoholic KOH forms with it *trichlorvinyl ethyl ether* $CCl_2 : CCl \cdot O \cdot C_2H_5$. Heated with alcohol, forms trichloracetal (Pergami).

Pentachlorether. Two isomerides:

(1) $CCl_3 \cdot CCl_2 \cdot O \cdot C_2H_5$; b.p. 190°–210° with decomposition; sp.gr. 1·645 (Jacobsen, Ber. 4, 217); by action of Cl upon trichlorvinyl ethyl ether (*v. supra*) (Busch, Ber. 11, 445).

(2) $CCl_3 \cdot CHCl \cdot O \cdot CH_2 \cdot CH_2Cl$; b.p. 235°; sp.gr. 1·577 at 80°. By action of PCl_5 on a compound of chloral and glycol chlorohydrin

$$CCl_3 \cdot CH(OH)O \cdot CH_2 \cdot CH_2Cl$$

(Henry, Ber. 7, 763).

Hexachlorether $CHCl_2 \cdot CHCl \cdot O \cdot CHCl \cdot CHCl_2$; b.p. 250°; by action of PCl_5 upon dichloraldehyde saturated with HCl (Paternò, Pisati, J. 1871, 508).

Octochlorether $C_4H_2Cl_8O$; from ethylidene oxychloride and Cl in sunlight (Roth, Ber. 8, 1017). Camphor-like smelling, volatile crystals.

Perchlorether $(C_2Cl_5)_2O$ (Regnault, Annalen, 34, 27); sp.gr. 1·900 at 14·5° (Malaguti, Ann. Chim. Phys. [3] 16, 4); the ultimate product of the action of Cl upon ether in sunlight, is a solid, forming orthorhombic scales, m.p. 69°, which possesses a smell like that of camphor. Decomposed by heating at 300° into C_2Cl_6 and $CCl_3 \cdot COCl$; with K_2S yields perchlorvinyl ether $(C_2Cl_3)_2O$, with liberation of S (Malaguti, Ann. Chim. Phys. [3] 16, 19). This body is a liquid, b.p. 210°, sp.gr. 1·652 at 21°, which combines with Cl in sunlight to form $(C_2Cl_6)_2O$, or with Br yielding $(C_2Cl_3Br_3)_2O$.

Ethyl peroxide $(C_2H_5)_4O_3$, produced by leading dry ozone into absolute ether (Berthelot, Bull. Soc. chim. ii. 36, 72), is a thick syrup which does not solidify at −40°, is partially volatile on heating, but easily explodes; is miscible with water, by which it is decomposed into C_2H_5OH and H_2O_2.

Ethyl phosphates.

1. *Normal ethyl phosphate* $(C_2H_5)_3PO_4$; b.p. 215°; sp.gr. 1·072 at 12°. By action of heat on lead diethyl phosphate $Pb(C_2H_5)_4(PO_4)_2$ (Vögeli, Annalen, 69, 190); from C_2H_5I and Ag_3PO_4 (Clermont, Ann. Chim. Phys. [3] 42, 330); from $POCl_3$ and C_2H_5ONa (Limpricht, Annalen, 134, 347); from P_2O_5 and absolute alcohol (Carius, *ibid.* 137, 121). Colourless liquid, miscible with and slowly decomposed by water, forming diethyl phosphoric acid.

2. *Diethyl phosphoric acid* $(C_2H_5)_2HPO_4$, a syrupy liquid obtained by action of P_2O_5 upon alcohol. It is a monobasic acid, and forms well-marked salts, *e.g.* $Ca[(C_2H_5)_2PO_4]_2$, crystalline needles; $Pb[(C_2H_5)_2PO_4]_2$ needles, m.p. 180°, soluble in water.

3. *Ethyl phosphoric acid* $H_2(C_2H_5)PO_4$, an oily liquid decomposed by heating, evolving $(C_2H_5)_2O$, C_2H_5OH, and C_2H_4. Equal parts of alcohol (95 p.c.) and syrupy H_3PO_4 are heated to 60° or 80°, diluted with water and neutralised with $BaCO_3$, filtered, the Ba salt allowed to crystallise, and then decomposed by H_2SO_4 (Pelouze, Ann. Chim. Phys. [2] 52, 37).

Also produced by action of P_2O_5 upon ether or alcohol or of syrupy H_3PO_4 upon ether (Vögeli, J. 1847-48, 694). Forms crystalline salts with the metals; of these the lead salt is least soluble.

Ethyl phosphites.

1. *Triethyl phosphite* $(C_2H_5)_3PO_3$; b.p. 191° (or 188° in stream of H); sp.gr. 1·075 at 15·5° (Railton, Chem. Soc. Trans. 1855, 7, 216); from PCl_3 and alcohol or sodium ethoxide.

An ethereal-smelling liquid, which absorbs O and is converted by PCl_5 into $PO(OC_2H_5)Cl_2$, PCl_3, and C_2H_5Cl (Geuther, Hertz. J. 1876, 207). By heating with $NaOC_2H_5$ yields $Na(C_2H_5)_2PO_3$; with $(C_2H_5O)_2O$, gives

$$H_2(C_2H_5)PO_3$$

(Jaehne, Annalen, 256, 269).

2. *Diethyl-phosphorous acid* $H(C_2H_5)_2PO_3$; b.p. 184°–185°; sp.gr. 1·0749 (15·5°/4°). From P_4O_6 and C_2H_5OH (Thorpe and North, Chem. Soc. Trans. 1890, 634); from PCl_3 and C_2H_5OH (Levitsky, J. Russ. Phys. Chem. Soc. 1903, 35, 211); from C_2H_5I and $Pb_3(PO_3)_2$ (Michaelis and Becker, Ber. 1897, 1005). Colourless mobile liquid with an alliaceous odour.

3. *Ethyl-phosphorous acid* $H_2(C_2H_5)PO_3$, very unstable syrupy liquid; obtained by action of PCl_3 upon weak alcohol (Wurtz, Ann. Chim. Phys. [3] 16, 218). The salts do not crystallise well, but are more stable than the acid.

Chloride of ethyl-phosphorous acid $C_2H_5POCl_2$; b.p. 117·5° (corr.); sp.gr. 1·30526 at 0°/4° (Thorpe, Chem. Soc. Trans. 37, 346); from PCl_3 and C_2H_5OH (Menschutkin, Annalen, 139, 343); decomposed by water into HCl, $C_2H_5 \cdot OH$, and H_3PO_3; also by heating to 165° into C_2H_5Cl, P, PCl_3, and P_2O_5 (Chambon, J. 1876, 205).

Diethyl pyro-phosphorous acid is not known, but the zinc salt $(C_2H_5)_2P_2O_5Zn$ is produced when $Zn(C_2H_5)_2$ is heated with P_2O_5 to 140° (Dilling, Zeitsch. Chem. 1867, 266).

Ethyl selenic acid $C_2H_5HSeO_4$, very unstable; produced from H_2SeO_4 and C_2H_5OH (Fabian, Annalen, Suppl. 1, 244). The salts are also unstable, the most permanent being the strontium salt; they can be crystallised with the ethyl-sulphuric acid salts.

Ethyl selenhydrate, *Ethyl selenomercaptan* C_2H_5SeH; b.p. 53·5°; sp.gr. 24°/4° 1·3954 (Tschugaeff, Ber. 1909, 42, 49). From ethyl iodide and sodium hydroselenide. Nauseous-smelling liquid.

Ethyl selenide, *Selenethyl* $(C_2H_5)_2Se$; b.p. 108°; discovered by Löwig (Pogg. Ann. 37, 552). By action of K_2Se upon $(C_2H_5)_2C_2O_4$ (L.); by action of $KC_2H_5SO_4$ upon K_2Se (Joy, Annalen, 86, 35; Rathke, *ibid.* 152, 210); the crude product is then distilled again with KOH, $C_2H_5HSO_4$, and a small piece of P or S (Pieverling, *ibid.* 185, 331; Ber. 9, 1469). A colourless mobile liquid with a not unpleasant smell, is insoluble in water, acts as a base; HCl precipitates from a solution in dilute HNO_3 an oily liquid $(C_2H_5)_2SeCl_2$, which gives with aqueous NH_3 a crystalline oxychloride $[(C_2H_5)_2Se]_2OCl_2$. Combines with C_2H_5I to form crystalline $(C_2H_5)_3SeI$ (Pieverling). This is a white substance resembling Epsom salts in appearance. The $(C_2H_5)_2SeCl_2$ forms double salts with several metallic chlorides; *e.g.*:

$$[(C_2H_5)_3SeCl]_2ZnCl_2.$$

Ethyl diselenide $(C_2H_5)_2Se_2$; b.p. 186°; formed as a by-product in the preparation of $(C_2H_5)_2Se$; was first obtained by Wöhler and Dean (Annalen, 97, 1) from $KC_2H_5SO_4$ and K_2Se_2 (Rathke, *ibid.* 152, 212); has an intensely disagreeable smell, and acts as a poison (Pieverling). A solution in dilute HNO_3 gives with HCl monoclinic crystals of $(C_2H_5)_2Se_2O_2(OH)_2Cl_2$, which are soluble in water, and are reduced by SO_2 to ethyl diselenide.

Ethoxy-selenyl chloride $C_2H_5O{\cdot}SeOCl$; m.p. 10°; b.p. 175°, not without decomposition. From $SeOCl_2$ and absolute alcohol. Heated in a tube to 200° yields Se, C_2H_5Cl, HCl, and H_2O (Michaelis and Landmann, Annalen, 241, 156).

Diethylselenite $SeO(OEt)_2$; b.p. 183°–185°, not without decomposition; sp.gr. 1·49 at 16·5°. From $SeOCl_2$ and NaOEt in dry ether at 180°–190°; also from Ag_2SeO_3, and C_2H_5I at 85° in sealed tube. A thick liquid, decomposed by water into C_2H_5OH and H_2SeO_3. Decomposed by heating in a tube at 200° with separation of Se (M. and L.).

Ammonium monoethylselenite

$$C_2H_5O{\cdot}SeO{\cdot}ONH_4;$$

a crystalline, very hygroscopic solid, formed by action of alcohol and ammonia upon SeO_2 at temperature of melting ice. It is soluble in alcohol, insoluble in ether (Divers and Hada, Chem. Soc. Trans. 75, 538).

Ethyl sulphates.

Mono-ethyl sulphate $C_2H_5HSO_4$ (*Ethyl-sulphuric acid*; *Sulphethylic acid*; *Sulphovinic acid*); sp.gr. 1·316 at 16°.

First noticed by Dabit (Crell's Ann. [1802] 1, 394); and again by Sertürner (Gilb. Ann. 60, 53; 64, 67, [1818–1820]; *see* also Heeren, Pogg. Ann. 7, 193; Hennel, Trans. Roy. Soc. 1826, 240; 1828, 365; Serullas, Ann. Chim. Phys. [2] 39, 153; Liebig and Wöhler, Pogg. Ann. 22, 487; Liebig, Annalen, 9, 17, 32; 13, 32, 38; Dumas and Boullay, Ann. Chim. Phys. [2] 36, 300).

Formed by action of sulphuric acid upon alcohol (Dabit, Sertürner, Serullas); also by absorption of ethylene in sulphuric acid (Hennel; Berthelot, Ann. Chim. Phys. [3] 43, 385); by heating ether with strong H_2SO_4 (Hennel; Magnus, Pogg. Ann. 27, 386); from S_2Cl_2 and alcohol (Heusser, Annalen, 151, 249); from $HO{\cdot}SO_2Cl$ and alcohol in the cold (on heating, this gives $C_2H_5O{\cdot}SO_2Cl$, Claesson, J. pr. Chem. [2] 19, 245).

Preparation.—A mixture of equal parts of absolute alcohol and strong sulphuric acid is heated for 4 hours on the water-bath; by this treatment 59 p.c. of the H_2SO_4 used is converted into mono-ethyl sulphate (Berthelot, Bull. Soc. chim. ii. 19, 295). By using 3 molecules alcohol and 1 molecule H_2SO_4 (*i.e.* 3 to 2 by weight), 77 p.c. of the sulphuric acid is utilised (Claesson, J. pr. Chem. [2] 19, 246). The mixture is diluted with water and neutralised with lead or barium carbonate, filtered, evaporated to crystallisation, the crystals dissolved in water, and the acid set free by means of H_2SO_4, or, when lead carbonate is used, by means of H_2S. The precipitated $BaSO_4$, $PbSO_4$, or PbS is removed by filtration, and the liquid evaporated *in vacuô* over sulphuric acid. Mono-ethyl sulphate is a syrupy liquid, very soluble in water, soluble also in alcohol, but insoluble in ether.

Heated with water, yields alcohol and sulphuric acid; on heating with alcohol to 140°, ether and H_2SO_4 are formed. Oxidising agents, *e.g.* MnO_2 or K_2CrO_4, give aldehyde (Jacquemin and Lies-Bodard, J. 1857, 345). The salts are very soluble in water, and can be heated in dilute solutions without decomposition, though in strong solution, or by prolonged heating, they are decomposed with formation of alcohol, a sulphate, and free H_2SO_4. This decomposition may be diminished by the addition of an alkali hydroxide or carbonate. By dry distillation, the salts yield 'heavy oil of wine,' a liquid containing diethyl sulphate and olefines. HCl gas yields C_2H_5Cl and a metallic sulphate (Köhler, Ber. 19, 11, 1929).

Salts (*v.* Marchand, Pogg. Ann. 32, 456; 41, 595). $LiC_2H_5SO_4,H_2O$; $NaC_2H_5SO_4,H_2O$; $KC_2H_5SO_4$, crystallises in anhydrous monoclinic plates, soluble in 0·8 part H_2O at 17°; (Schabus, J. 1854, 560; Marignac, J. 1855, 608).

$Mg(C_2H_5SO_4)_2,4H_2O$; $Ca(C_2H_5SO_4)_2,2H_2O$, forms monoclinic laminæ, soluble in 0·8 part water at 17° (M.); $Ba(C_2H_5SO_4)_2,2H_2O$, monoclinic plates, sp.gr. 2·080 at 21·7°, soluble in 0·92 parts of water at 17° (M.); $Pb(C_2H_5SO_4)_2,2H_2O$; large rhombic tables — $Pb(C_2H_5SO_4)_2,PbO$; amorphous; soluble in 0·54 part H_2O at 17°.

Diethyl sulphate $(C_2H_5)_2SO_4$; sp.gr. 1·1837 at 19° (Claesson, J. pr. Chem. [2] 19, 257); b.p. 208° (with decomposition), 113·5° at 31 mm., 118° at 40 mm., 120·5° at 45 mm. (Villiers, Bull. Soc. chim. ii. 34, 26); m.p. about −24·5° (V.); occurs in 'heavy oil of wine.' Formed by leading SO_3 vapour into absolute ether (Weltzien, Annalen, 66, 117); in small quantity by distillation of $C_2H_5HSO_4$; by

dropping alcohol into chloride of ethyl sulphuric acid $C_2H_5O{\cdot}SO_2Cl$, or by action of H_2SO_4 upon alcohol (Claesson); from Ag_2SO_4 and C_2H_5I (Stempnewsky, Ber. 11, 514). A mixture of 1 vol. absolute alcohol and 2 vols. H_2SO_4 is distilled slowly *in vacuô* (Villiers). Absolute alcohol is mixed with Nordhausen sulphuric acid, the ether separated by means of $CHCl_3$, and the product distilled *in vacuô* (Claesson and Lundvall, Ber. 13, 1699).

Is an oily liquid, with an odour like that of peppermint; insoluble in water, and slowly decomposed by that liquid even in the cold; when heated with water, yields alcohol, H_2SO_4 and $C_2H_5HSO_4$. Heated with alcohol, forms ether and $C_2H_5HSO_4$; warm baryta water forms alcohol and $Ba(C_2H_5SO_4)_2$ (Villiers).

Chloride of ethyl sulphuric acid $C_2H_5O{\cdot}SO_2Cl$; b.p. 151°–154° (corr.) (Claesson, J. pr. Chem. [2] 19, 248), with slight decomposition; 93°–95° at 100 mm. (Müller, Ber. 6, 227). From C_2H_5Cl and SO_3, together with isomerides (*v. Ethyl chloride*, p. 356); by dropping alcohol into SO_2Cl_2 (not *vice versâ*; diethyl sulphate is then formed) (Behrend, J. pr. Chem. [2] 15, 28); from a salt of ethyl sulphuric acid and PCl_5 (Purgold, Ber. 6, 505); from ethyl chloroformate $Cl{\cdot}CO_2C_2H_5$ and fuming sulphuric acid (Wilm, Ber. 6, 505); by passing C_2H_4 into HSO_3Cl, $SO_4H{\cdot}C_2H_4{\cdot}SO_2Cl$ is also produced (Müller, *ibid.* 6, 227).

A liquid with an irritating smell, exciting tears, and decomposed by contact with water into HCl, H_2SO_4 and alcohol. When the chloride is added to methyl alcohol or ethyl alcohol, ethyl sulphuric acid and CH_3Cl or C_2H_5Cl are produced; with amyl alcohol, amyl sulphuric acid and ethyl chloride are formed (Müller). If, on the other hand, absolute alcohol is dropped into the chloride, diethyl sulphate is produced (Claesson).

Bromethyl sulphuric acid

$$CH_2Br{\cdot}CH_2{\cdot}OSO_2OH(?);$$

from ethylene bromide and SO_3 (Wroblewski, Zeitsch. Chem. 1868, 563). The barium salt is anhydrous, and is decomposed by continued heating with water, with separation of $BaSO_4$ and formation of glycol (Beilstein and Wiegand, Ber. 15, 1370). An isomeric body

$$CH_3{\cdot}CHBr{\cdot}OSO_2{\cdot}OH(?)$$

is formed by acting upon ethylene bromide with Ag_2SO_4 and water (B. and W.); the barium salt is very soluble in water, and its solution decomposes on warming into $BaSO_4$, HBr, and glycol.

Dibromo-diethyl sulphate $(CH_2Br{\cdot}CH_2)_2SO_4$; by action of ethylene bromide upon Ag_2SO_4 in presence of benzene (Beilstein and Wiegand, Annalen, 15, 1369); a heavy oil insoluble in water, soluble in benzene and ether, decomposed on heating. Heated with water, yields bromide of ethyl sulphuric acid, and finally HBr, H_2SO_4, and glycol.

Ethyl sulphites.

Mono-ethyl sulphite $C_2H_5O{\cdot}SO{\cdot}OH$, *Ethyl sulphurous acid, Hyposulphtheylic acid.* The potassium salt $KC_2H_5SO_3$ is obtained by passing SO_2 into a well-cooled solution of $NaOC_2H_5$ in absolute alcohol (Rosenheim and Liebknecht, Ber. 1898, 408). The ammonium salt is prepared by passing NH_3 followed by SO_2 into absolute alcohol (Divers and Ogawa, Chem. Soc. Trans. 1899, 535). The alkali salts are very unstable in the solid state decomposing with evolution of SO_2. Dilute mineral acids bring about this change in solution; ethyl iodide and alcohol at 150° yield ethyl sulphonate (*q.v.*). By treatment with PCl_5, diethyl sulphite yields the *chloride of ethyl sulphurous acid* $C_2H_5O.SOCl$ which boils at 122°, is decomposed by water into HCl, SO_2, and alcohol, and gives, by further action of PCl_5 at 180°, thionyl chloride, C_2H_5Cl, and $POCl_3$ (Michaelis and Wagner, Ber. 7, 1074). Ethyl sulphurous acid is isomeric with ethyl sulphonic acid $C_2H_5{\cdot}SO_2{\cdot}OH$ (*q.v.*).

Diethyl sulphite $C_2H_5O{\cdot}SO{\cdot}OC_2H_5$; sp.gr. 1·1063 at 0° (Carius, J. pr. Chem. [2] 2, 279); b.p. 161·3°. From alcohol and S_2Cl_2; 18 parts of absolute alcohol are mixed with 50 parts of S_2Cl_2, previously warmed to 60°; the mixture is kept at this temperature for an hour, and then distilled; the portion boiling above 150° is redistilled (Warlitz, Annalen, 143, 74).

A colourless liquid, with mint-like odour, miscible with alcohol and ether; insoluble in water. Decomposed by water; with PCl_5, yields a chloride C_2H_5OSOCl, which, on distillation, splits up into C_2H_5Cl and SO_2 (Geuther, Annalen, 224, 223; Michaelis and Wagner, Ber. 7, 1074). Decomposed by KOH into potassium ethyl sulphonate (Rosenheim and Liebknecht, *ibid.* 31, 405). Decomposes at 200° into SO_2 and ether (Prinz, Annalen, 223, 374); or by heating with $SOCl_2$, to 120°, into SO_2 and C_2H_5Cl (Geuther).

Ethyl sulphydrate C_2H_5SH. *Mercaptan, Ethyl mercaptan*; b.p. 36·2° (Nasini, Ber. 15, 2882); sp.gr. 0·83907 at 20°/4° (N.), 0·835 at 21°. By distilling $Ba(C_2H_5SO_4)_2$ with $Ba(HS)_2$ (Zeise, Annalen, 11, 1); by action of KHS upon C_2H_5Cl (Regnault, Ann. Chim. Phys. [2] 71, 390); by heating absolute alcohol saturated with SO_2 in a sealed tube, there are also formed $C_2H_5HSO_4$, $(C_2H_5)_2O$, and H_2SO_4 (Endemann, Annalen, 140, 336); from P_2S_5 and alcohol (Kekulé, Annalen, 90, 310). It is best prepared by saturating a solution of KOH, sp.gr. 1·3, with H_2S, mixing with a solution of $Ca(C_2H_5SO_4)_2$ (also of sp.gr. 1·3), and distilling on water-bath (Liebig, Annalen, 11, 14); according to Claesson (J. pr. Chem. [2] 15, 193), $(C_2H_5)_2S$ is also formed; NaC_2H_5S is prepared from the product of this action, the alcoholic solution evaporated to dryness, the $(C_2H_5)_2S$ removed by means of benzene, and the C_2H_5NaS decomposed by dilute H_2SO_4.

It is a colourless liquid with a penetrating garlic-like smell, slightly soluble in water, from which it crystallises on evaporation with $18H_2O$, m.p. 12° (Claesson). It gives with bromine C_2H_5Br, HBr, and BrS (Friedel, Ladenburg, Annalen, 145, 189). HNO_3 forms $C_2H_5SO_2{\cdot}SC_2H_5$, or, if the acid be stronger, ethyl sulphonic acid. Treated with Cu powder, loses its disagreeable odour, but is considerably decomposed thereby (Finckh).

It forms crystalline compounds with $SiCl_4$ (Demarcay, Bull. Soc. chim. [2] 20, 127). It absorbs NO, forming a dark-red solution.

The hydrogen of mercaptan is replaceable by metals forming mercaptides; *e.g.* C_2H_5KS and $Hg(C_2H_5S)_2$, transparent plates, m.p. 76°–77° (Otto, Ber. 13, 1290; 15, 125), very slightly soluble in cold alcohol, soluble in 12–15 parts

hot alcohol (Liebig, Annalen, 11, 17); gives with HNO_3 the nitrate $Hg(C_2H_5S)NO_3$ (Hofmann and Rabe, Zeitsch. anorg. Chem. 17, 26); $Pb(C_2H_5S)_2$, yellow precipitate, formed when $Pb(C_2H_3O_2)_2$ and C_2H_5HS are mixed in alcoholic solutions. $As(C_2H_5S)_3$, a foul-smelling oil formed from $AsCl_3$ and C_2H_5NaS, decomposed by heat into As and $(C_2H_5)_2S_2$. $Pt(C_2H_5S)_2$ pale-yellow precipitate (Zeise).

Ethyl sulphide $(C_2H_5)_2S$; b.p. 91° (Pierre, J. 1851, 51), 91·9° at 754·7 mm. (Beckmann, J. pr. Chem. [2] 17, 451), 92·2°–93° (corr.) at 754 mm. (Nasini, Ber. 15, 2882); sp.gr. 0·8367 at 0° (Pierre), 0·83676 at 20°/4° (N.). From K_2S and C_2H_5Cl (Regnault, Ann. Chim. Phys. [2] 71, 387); from $Zn(C_2H_5)_2$ and $SOCl_2$ (Gauhe, Annalen, 143, 266); from KHS and $KC_2H_5SO_4$ in alcohol (Hobson, Chem. Soc. Trans. 10, 56); also from P_2S_5 and $(C_2H_5)_2O$ (Beckmann). To prepare the pure sulphide, heat the crude sulphide with Cu powder to 260°–280° (Finckh, Ber. 1894, 1239).

It is a colourless liquid with strong garlic-like smell, insoluble in water. Brühl states that in the pure state it has an ethereal odour. Chlorine acts upon it in the dark, forming substitution products: (1) $(C_2H_3Cl_2)_2S$, yellow liquid, b.p. 167°–172°, sp.gr. 1·547 at 12°; (2) $(C_2H_2Cl_3)_2S$, b.p. 189°–192°, sp.gr. 1·219 at 13·5°; (3) $(C_2HCl_4)_2S$, b.p. 217°–222°. By prolonged action of chlorine, C_2Cl_6 is formed, and possibly $(C_2Cl_5)_2S$ (Riche, Ann. Chim. Phys. [3] 43, 283; Annalen, 92, 358). $(C_2H_2Cl_3)_2S$ also results from action of chlorine upon $(C_2H_3Cl_2)_2S$, which can be obtained from C_2H_4 and Cl_2S_2 (Guthrie, Annalen, 116, 241). Bromine forms $(C_2H_5)_2SBr_2$, a yellowish-red unstable body, which, by the action of KI, yields $(C_2H_5)_2SI_2$, a black liquid (Rathke, Annalen, 152, 214).

Ethyl sulphide combines with many metallic chlorides to form crystalline compounds, *e.g.* $(C_2H_5)_2S{\cdot}HgCl_2$, white crystals, soluble in alcohol and ether, m.p. 119°; $(C_2H_5)_2S{\cdot}HgI_2$, yellow needles, m.p. 110°; $2(C_2H_5)_2S{\cdot}TiCl_3$, dark-red crystals (Demarcay). (For addition compounds, *see* Abel, Zeitsch. physiol. Chem. 20, 268; Werner, Zeitsch. anorg. Chem. 15, 14; 17, 101; Smiles, Chem. Soc. Trans. 1900, 164.)

Nitric acid (of sp.gr. 1·2) forms *ethyl sulphoxide* or *diethyl sulphine oxide* $(C_2H_5)_2SO$, a soluble oily liquid, solid at low temperatures, and decomposed by heating. Fuming nitric acid converts this into *diethyl sulphone* $(C_2H_5)_2SO_2$; b.p. 248°; m.p. 70°–72° (Oefele, Annalen, 127, 370; 132, 88); $R_\infty = 47{\cdot}53$ (Kanonnikow, J. Russ. Phys. Chem. Soc. 15, 451); also formed from $Pb(C_2H_5)_4$ and SO_2 (Frankland and Lawrence, Chem. Soc. Trans. 35, 244), and from $(C_2H_5)_2S$, and a solution of $KMnO_4$ (O.). Rhombic plates, soluble in 6·4 parts water at 16°.

Triethyl sulphine $(C_2H_5)_3S$ forms compounds in which it plays the part of a univalent radicle.

$(C_2H_5)_3SI$ from $(C_2H_5)_2S$, C_2H_5I, and H_2O (Oefele, Annalen, 132, 82); from HI and $(C_2H_5)_2S$ or HI and C_2H_5HS, or C_2H_5I and C_2H_5HS (Cahours, *ibid.* 135, 352; 136, 151); forms rhombic plates of disagreeable odour, and soluble in water. By action of Ag_2O, yields *triethyl sulphine hydroxide* $(C_2H_5)_3SOH$, a strong base; displaces NH_4, and has caustic action on the skin; it forms a crystalline deliquescent mass, which unites with acids to form deliquescent salts yielding double compounds with many metallic salts; *e.g.*:

$$PtCl_4{\cdot}2(C_2H_5)_2SCl,$$

dark-reddish prisms, soluble at 20·7° in 30 parts of water (Dehn, Annalen, Suppl. 4, 90; Jörgensen, J. pr. Chem. [2] 6, 82; Kraut, Annalen, 210, 321).

When $(C_2H_5)_2S$ is heated with CH_3I, *diethyl-methyl sulphine iodide* $(C_2H_5)_2CH_3SI$, an unstable non-crystalline body, is formed, from which other salts can be obtained; the chloride $(C_2H_5)_2CH_3SCl$ forms many double salts (Krüger, J. pr. Chem. [2] 14, 195). The isomeride, *ethyl-methylethyl sulphine iodide*, prepared from $C_2H_5CH_3S$ and C_2H_5I, is crystalline (Krüger).

Ethyl disulphide $(C_2H_5)_2S_2$; b.p. 152·8°–153·4° (corr.) at 730 mm. (Nasini, Ber. 15, 2882); sp.gr. 0·99267 at 20°/4° (N.). By distillation of $KC_2H_5SO_4$ with K_2S_2 and water (Zeise, Annalen, 11, 1; Morin, *ibid.* 32, 267; Löwig, Kopp, *ibid.* 35, 345; Cahours, *ibid.* 61, 98); by action of I upon a slight excess of a solution of C_2H_5NaS (Kekulé; Linnemann, *ibid.* 123, 279); by action of S upon C_2H_5SNa (Böttger, *ibid.* 223, 348); by distilling liquid thioacetaldehyde (Klinger, Ber. 32, 2195).

A colourless liquid, with garlic-like smell, very slightly soluble in water; with dilute HNO_3, gives $(C_2H_5)_2S_2O_2$, an oily liquid, which may be regarded as the ethyl salt of ethyl thiosulphonic acid $C_2H_5SO_2SC_2H_5$.

Ethyl trisulphide $(C_2H_5)_2S_3$, from K_2S_3 and $KC_2H_5SO_4$ (Cahours, Bull. Soc. chim. [2] 25, 184); also from $(C_2H_5)_2S_2$ and S (H. Müller); a colourless liquid, with unpleasant smell.

Ethyl tetrasulphide $(C_2H_5)_2S_4$; from S_4Cl_2 and C_2H_5SH (Claesson, J. pr. Chem. [2] 15, 214); a heavy oily liquid, with disagreeable odour.

Ethyl pentasulphide $(C_2H_5)_2S_5$; by heating $(C_2H_5)_2S_4$ and S at 150°; a tough elastic solid.

Ethyl sulphinic acid $C_2H_5HSO_2$; by action of $Zn(C_2H_5)_2$ upon SO_2 (Wischin, Annalen, 139, 364; Hobson, Chem. Soc. Trans. 1858, 10, 58); the sodium salt is produced by oxidation of sodium mercaptide by dry oxygen (Claesson, J. pr. Chem. [2] 15, 199). The free acid is a syrupy liquid with a sweet taste; by action of HNO_3, yields ethyl sulphonic acid and $(C_2H_5SO_2)_3NO$, crystals, m.p. 81·5°, very slightly soluble in water (Zuckschwerdt, Annalen, 174, 308). Forms salts, of which $NaC_2H_5SO_2$ crystallises from alcohol in anhydrous crystals (C.); the lead salt was prepared from $Pb(C_2H_5)_4$ and SO_2 by Frankland and Lawrance (Chem. Soc. Trans. 35, 244).

Ethyl sulphonic acid $C_2H_5{\cdot}SO_2{\cdot}OH$ by the oxidation of C_2H_5SH (Löwig and Weidmann, Pogg. Ann. 49, 329; Kopp, Annalen, 35, 346), C_2H_5CNS or of $(C_2H_5)_2S_2$ (Muspratt, Chem. Soc. Trans. 1849, 1, 45) by HNO_3; from C_2H_5I and K_2SO_3 (Graebe, Annalen, 146, 37). By heating ethylene sulphonic acid with P and HI at 170° (Kohler, Amer. Chem. J. 20, 688); by oxidation of C_2H_5CNS with hypochlorites (De Coninck, Compt. rend. 126, 838); by action of conc. HNO_3 upon mercury mercaptide nitrate (Hofmann and Rabe, Zeitsch. anorg. Chem. 17, 26). The acid is a crystalline deliquescent body; by action of ICl_3 at 150°, we get dichlorethyl sulphonic acid; excess of ICl_3 gives C_2Cl_6 (Spring and Wessinger, Ber.

15, 445); unites with bases to form salts. (For halogen derivatives, *see* Kohler, Amer. Chem. J. 19, 737; 20, 690; 21, 361. For salts, *see* Rosenheim and Liebknecht, Ber. 31, 412.)

Ethyl sulphonate $C_2H_5{\cdot}SO_2{\cdot}OC_2H_5$; b.p. 213·4° (corr.); sp.gr. 1·1712 at 0°/0° 1·1452 at 20°/4° (Nasini, Ber. 15, 2884); by action of ethyl sulphonic chloride $C_2H_5SO_2Cl$ and C_2H_5NaO (Carius, J. 1870, 726; J. pr. Chem. [2] 2, 262); from C_2H_5I and silver sulphite or sodium ethyl sulphite (*q.v.*).

Ethyl sulphonic chloride $C_2H_5SO_2Cl$; b.p. 177·5° (corr.) (Carius), 171° (Otto, Ber. 15, 122); sp.gr. 1·357 at 22·5° (C.); by action of PCl_3 on $NaC_2H_5SO_3$ (Gerhardt and Chancel, Compt. rend. 35, 690); by action of Cl upon ethyl oxysulphide (S. and W. *l.c.*). Colourless liquid, with unpleasant smell.

Ethyl thiocyanate C_2H_5SCN; b.p. 143° (Berthelot, Compt. rend. 130, 444), 146° (corr.) (Buff, Ber. 1, 206); sp.gr. 1·033 at 0°, 1·0126 at 19°, 0·8698 at 146° (B.); by action of KCNS upon $KC_2H_5SO_4$ (Cahours, Ann. Chim. Phys. [3] 18, 264; Annalen, 61, 95), or C_2H_5Cl (Löwig, Pogg. Ann. 67, 101), or C_2H_5I (Johnson and Levy, Amer. Chem. J. 1907, 38, 456); from Et_2SO_4 and KCNS, yield 87 p.c. (Walden, Ber. 1907, 3214).

A mobile liquid with unpleasant odour, insoluble in water, miscible with alcohol or ether; by action of sodium forms NaCN and $(C_2H_5)_2S$ (Hofmann, Ber. 1, 184); by heating with solution of KOH, yields $(C_2H_5)_2S_2$, KCN, and KCNO (Brüning, Annalen, 104, 198); with alcoholic KOH, forms $(C_2H_5)_2S_2$, CO_2, NH_3, but no KCNS (Löwig), but with alcoholic KHS yields C_2H_5HS and KCNS (L.). Decomposed by hot solution of bleaching powder, yielding CO_2, N, $EtO{\cdot}SO_2{\cdot}OH$, and H_2SO_4. NaClO and NaOH hot, yield $(EtO)_2SO_2$ and NaCN. Further action gives Et_2S_2, NaCN, and NaCNO, if all the hypochlorite is used up. By action of aqueous NH_3 at 100°, it yields $(C_2H_5)_2S_2$, NH_4CN, urea, oxalic acid, and other products (Kremer, J. 1858, 401; Jeanjean, J. 1862, 364). By passing Cl into it, there results $(CNCl)_3$ and a liquid $C_2H_3SCl_3$, b.p. 134°–135° (James, J. pr. Chem. [2] 30, 316). A chlorine substitution product C_2H_4ClSCN was obtained by James (*ibid.* [2] 20, 352) by heating C_2H_4ClBr with KCNS and alcohol; an oil heavier than water, with unpleasant smell; b.p. 202°–203°; m.p. below −20°.

Ethyl thiocyanate forms compounds with HCl, HBr, and HI (Henry, J. 1868, 652; Glutz, Annalen, 153, 312). (For many other compounds, *see* Wheeler and Johnson, Amer. Chem. J. 26, 345; J. Amer. Chem. Soc. 24, 680; Wheeler and Jamieson, *ibid.* 24, 743; Wheeler and Merriam, *ibid.* 24, 439.)

Ethyl *iso*thiocyanate C_2H_5NCS (L.), *Ethylthiocarbimide, mustard oil*; b.p. 134°; sp.gr. 1·0192 at 0°, 0·9972 at 22°, 0·8763 at 133·2° (Buff, Ber. 1, 206); by action of C_2H_5NCO upon P_2S_5 (Michael and Palmer, Amer. Chem. J. 6, 259), also in very small quantity when $Hg(CNS)_2$ is heated with C_2H_5I (Michael, *ibid.* 1, 417), also by heating $CSCl_2$ and $(C_2H_5)NH_2$ (Rathke, Annalen, 167, 211). A solution of ethylamine in alcohol is treated with CS_2, when crystals of ethyl ammonium ethyl dithiocarbamate separate out, $2(C_2H_5)NH_2+CS_2=(C_2H_5)NH{\cdot}CS{\cdot}S{\cdot}NH_3(C_2H_5)$. A solution of this body is then treated with $HgCl_2$, when the mercury compound is precipitated:

$$(C_2H_5)NH{\cdot}CS{\cdot}S{\cdot}NH_3(C_2H_5)+HgCl_2 = 2(C_2H_5)H_2NCl+[NH(C_2H_5)CS_2]_2Hg.$$

On distillation, this body yields the mustard oil, HgS and H_2S (Hofmann, Ber. 1, 171; 2, 452). Delépine (Compt. rend. 144, 1125) improves the yield of dithiocarbamate by using 1 molecule each of CS_2, amine, and soda, and then distilling with basic lead acetate in place of $HgCl_2$. Mustard oil is a liquid with very disagreeable smell, and in contact with the skin produces a burning sensation (Hofmann, Ber. 1, 26); with absolute alcohol forms **monoethyl thiourethane** $(C_2H_5)NH{\cdot}CS{\cdot}OC_2H_5$, a liquid, b.p. 204°–208°; with aldehyde ammonia yields the compound $C_7H_{15}N_3S$, m.p. 135°–136° (Dixon, Chem. Soc. Trans. 1888, 414).

Thiocarbimides react with phenylhydrazine, yielding thiosemicarbazides (Marckwald). With Br in chloroform a ring compound, $C_2OS_2(NEt)_2$, melting at 45°, is formed (Freund and Bachrach, Annalen, 285, 184).

Ethyl thiophens $C_4SH_3(C_2H_5)$.

2-*Ethyl thiophen*; b.p. 132°–134° (corr.), sp.gr. 0·990 at 24°. By action of C_2H_5Br and Na upon C_4SH_3I (Meyer and Kreis, Ber. 17, 1560); also by action of Br upon thiophen, C_2H_5Br and Na (Schleicher, *ibid.* 18, 3015; *ibid.* 19, 671).

3-*Ethyl thiophen*; b.p. 135°–136°; sp.gr. 1·0012 at 16°. By heating ethyl succinic acid with P_2S_3 (Damsky, Ber. 19, 3284; Gerlach, Annalen, 267, 146).

Di-ethyl thiophen; b.p. 181°; sp.gr. 0·962 at 14°/14°. An oil obtained by action of Na upon C_2H_5I and iodoethylthiophen (Muhlert, Ber. 19, 633).

Ethyl telluride $(C_2H_5)_2Te$, *Tellurethyl*; b.p. 137°–138° (Marquardt and Michaelis, Ber. 21, 2045; Heeren, J. 1861, 565); from K_2Te and $KC_2H_5SO_4$ (Wöhler, Annalen, 84, 69; 35, 111; Mallet, Chem. Soc. Trans. 1853, 5, 71). A heavy, viscid, reddish-yellow liquid, with a very unpleasant smell, burns in air with blue flame, evolving fumes of TeO_2; hardly soluble in water, and oxidised by exposure to air; is poisonous. HNO_3 forms $(C_2H_5)_2Te,HNO_3$ (monoclinic prisms). Strong HCl precipitates the oily compound $(C_2H_5)_2TeCl_2$ from a solution of the nitrate; ammonia converts this into $[(C_2H_5)_2Te]_2Cl_2O$ (hexagonal prisms), which, when treated with Ag_2SO_4, yields

$$[(C_2H_5)_2Te]_2,H_2SO_4$$

(colourless prisms). By action of Ag_2O upon a solution of the chloride, $(C_2H_5)_2TeO$ is produced, which decomposes on concentration.

When $(C_2H_5)_2Te$ is acted upon by C_2H_5I, *triethyl tellurium iodide* $(C_2H_5)_3TeI$ is formed, m.p. 90°–92° (Cahours, Bull. Soc. chim. [2] 4, 40), which crystallises in yellow prisms.

Ethyl ditelluride $(C_2H_5)_2Te_2$ is said to be formed in the preparation of $(C_2H_5)_2Te$, and to be a dark-red liquid, with high boiling-point.

Ethylamines.

Compounds in which one or more atoms of H in NH_3 are replaced by C_2H_5.

Ethylamine $C_2H_5{\cdot}NH_2$; b.p. 18·7°, sp.gr. 0·6964 at 8°, 0·708 at 2° (Hofmann, Ber. 22, 699); m.p. −85·2°, b.p. 19° to 20° (Ladenburg

and Krugel); sp.gr. 0·7013 at 4°, 0·6892 at 15° (Perkin); crit. temp. 185·2° (Schmidt); H.C.=408·5 Cals. (Berthelot, Ann. Chim. Phys. [5] 23, 244). From ethyl carbimide and KOH (Wurtz, Annalen, 71, 330; also Compt. rend. 28, 223); from C_2H_5Br and NH_3 (Hofmann, Annalen, 74, 159); by the putrefaction of yeast and of flour (Hesse, J. 1857, 403; Sullivan, J. 1858, 231); by heating alcohol with NH_4Cl at 300° (Berthelot, Ann. Chim. Phys. [3] 38, 63); by action of nascent H upon acetonitrile (Mendius, Annalen, 121, 142). It is also produced in the dry distillation of the residues from beet-root in sugar manufacture (Duvillier and Buisine, Ann. Chim. Phys. [5] 23, 317); by action of $KC_2H_5SO_4$ upon alcoholic NH_3 at 120° (Erlenmeyer and Carl, J. 1875, 617); by action of Na upon $CH_3{\cdot}CONH_2$ in boiling amyl alcohol (Guerbet, Compt. rend. 129, 62); from EtOH and phospham at 225°–250° (Vidal, D. R. P. 64346); by action of Zn filings and HCl in the cold on aldehyde ammonia (Trillat and Fayollat) (Jean); by electrolytic reduction of nitroethane in H_2SO_4 at 70°–75° (Pieron, Bull. Soc. chim. [3], 21, 784).

Preparation. — (1) 1 volume of ethyl nitrate $C_2H_5NO_3$ is treated with 3 volumes of alcoholic ammonia for 12 hours at 100°; the free bases are separated from the NH_3 by neutralising with H_2SO_4 or HCl and extracting with alcohol; the sulphates or chlorides are then decomposed by NaOH, and the free bases combined with picric acid and crystallised. The picrate of $(C_2H_5)_3N$ separates first, in yellow needles, then the $C_2H_5NH_2$ salt in brown prisms; the picrates are then separated and decomposed by HCl, and the bases liberated by KOH (Carey Lea, Chem. News, 5, 118).

(2) Crude C_2H_5Cl, from manufacture of chloral, is heated for an hour with 3 times its volume of alcohol (95 p.c.) previously saturated with ammonia, in an iron vessel heated by a water-bath. On cooling, the NH_4Cl is filtered off, and the remainder distilled until free from NH_3 and alcohol, the residue (hydrochlorides of mon-, di-, and tri-ethylamine, mixed with a little NH_4Cl) is treated with a strong solution of NaOH, and the liquid drawn off and dried by means of solid NaOH; it consists of a mixture of the three bases; ethyl oxalate is then added, and the $(C_2H_5)_3N$, which is unacted upon, is distilled off; the residue consists of a mixture of solid *diethyl oxamide* $C_2O_2(NHC_2H_5)_2$ and liquid *ethyl diethyloxamate* $C_2O_2N(C_2H_5)_2OC_2H_5$, which are separated and the diethyl oxamide, after recrystallising from hot water, decomposed with KOH (Hofmann, Ber. 3, 109, 776; also Duvillier and Buisine, Compt. rend. 88, 31).

Properties.—Is a mobile liquid, with strong ammoniacal odour, is strongly caustic, and has an alkaline reaction; burns with yellow flame, is miscible in all proportions with water, displaces NH_3 from its salts, and, like ammonia, precipitates metallic hydroxides and oxides from salts. It, however, dissolves the hydroxides of Al (Wurtz), Au, and Ru (Carey Lea), and does not dissolve those of Cd, Ni, and Co. The chloride is decomposed on distillation into $C_2H_5NH_2$, $(C_2H_5)_2NH$, NH_3, C_2H_4, and C_2H_5Cl (Fileti and Piccini, Ber. 12, 1508). CrO_3 oxidises ethylamine to aldehyde and N (Carstanjen, J. 1862, 330).

Caro's acid oxidises $EtNH_2$ yielding CH_3COOH, CH_3CN, $CH_2CH{:}NOH$, nitroethane, and $CH_3C(OH)NOH$ (Bamberger, Ber. 35, 4293). It forms a compound C_2H_5NHK (Titherley).

Salts (*v.* Wurtz, Annalen, 76, 329).—$(C_2H_5)NH_2,HCl$, deliquescent plates; m.p. 76°–80°; b.p. 315°–320° (with decomposition); sp.gr. 1·2045 at 21°/4° (Schiff and Monsacchi); molecular refract. 35·97 (calc. 35·95) (Kanonnikow, J. pr. Chem. [2] 31, 347); soluble in alcohol; soluble in 0·42 part of water at 17° (S. and M. Zeitsch. physikal. Chem. 24, 513). Prepared by heating 1 volume of C_2H_5Cl with 3 volumes alcoholic ammonia to 100° (Groves, Chem. Soc. Trans. 1861, 13, 331). The hydrochloride and hydroiodide exhibit isodimorphism; both are monoclinic at ordinary temperatures, changing at higher temperatures to uniaxial modifications. $C_2H_5NH_2,HgCl_2$, by action of alcoholic $HgCl_2$ on alcoholic $C_2H_5NH_2$; a crystalline precipitate, soluble in hot HCl solution. With excess of $HgCl_2$ in aqueous solution a white precipitate

$$2C_2H_5NH_2,HgCl_2+2HgO$$

is thrown down; by heating $C_2H_5NH_2$ with excess of $HgCl_2$, a yellow precipitate

$$ClHg{\cdot}OHg{\cdot}NH{\cdot}C_2H_5$$

separates; whilst a crystallisable compound $ClHg{\cdot}NH{\cdot}C_2H_5$ remains in solution (Köhler, Ber. 12, 2308). $2C_2H_5NH_2,PtCl_2$, yellow powder, combines with $(C_2H_5)NH_2$, and forms

$$4C_2H_5NH_2,PtCl_2,2H_2O,$$

colourless crystals, soluble in water.

$(C_2H_5{\cdot}NH_2,HCl)_2,PtCl_4$, orange-yellow flat rhombohedrons (Weltzien, Annalen, 93, 272), hexagonal rhombohedrons (Topsoë, J. 1883, 619); sp.gr. 2·255 at 19°/4° (Clarke, Ber. 12, 1399). $C_2H_5NH_2,HCl,AuCl_3$, golden-yellow monoclinic prisms, soluble in water (T.).

$(C_2H_5NH_2)_2,H_2SO_4$, deliquescent body, soluble in alcohol; forms double salts with other sulphates, *e.g.* ethyl-ammonium alum

$$(C_2H_5NH_2)_2,H_2SO_4,Al_2(SO_4)_3,24H_2O,$$

octahedral crystals, soluble at 25° in 6·89 parts of water.

Ethylchloramine C_2H_5NHCl. A very pungent-smelling oil; sp.gr. 1·067 at 0°; formed by action of NaClO upon $C_2H_5NH_2,HCl$. Heated with HCl, yields ethylamine (Berg, Ann. Chim. Phys. [7] 3, 319).

Ethyl dichloramine, ethylnitrogenchloride $C_2H_5{\cdot}NCl_2$; b.p. 88°–89° at 762 mm.; sp.gr. 1·230 at 15°; by passing Cl through aqueous $C_2H_5NH_2$ (Wurtz, Compt. rend. 11, 810), prepared by distilling a mixture of $C_2H_5NH_2,HCl$ with 2½ times its weight of bleaching powder and a little water (Tscherniak, Ber. 9, 146), a yellow oily liquid with a penetrating smell, insoluble in water and acids, decomposes on long standing into HCl, NH_4Cl, $C_2H_5NH_2,HCl$, $CHCl_3$, CH_3CN, and $CH_3{\cdot}COCl$ (Köhler, Ber. 12, 1870). The pure substance keeps unchanged for long periods under water (Tscherniak, *ibid.* 12, 2129). Alkalis decompose it into acetic acid and NH_3; behaves towards many bodies as free Cl. $Zn(C_2H_5)_2$ forms $(C_2H_5)_3N$ and $ZnCl_2$.

Ethyl di-iodoamine $C_2H_5NI_2$, and *Ethyl dibromamine* $C_2H_5NBr_2$, are formed similarly; the former is a dark-blue liquid (Wurtz).

Ethyl nitramine $C_2H_5NH{\cdot}NO_2$; m.p. +6°; sp.gr. 1·1675 at 15°. A colourless liquid, with an acid reaction, prepared by the action of NH_2 upon diethyl dinitro-oxamide. It gives two classes of alkyl derivatives (Umbgrove and Franchimont, Rec. trav. chim. 16, 388). It is also formed from methyl ethylcarbamate and conc. HNO_3 (Franchimont and Klobbie, *ibid.* 7, 356).

Nitroethylisonitramine $CH_3{\cdot}CHNO_2{\cdot}N(OH)NO$ is obtained by the action of NO upon the Na derivative of nitroethane. It forms metallic salts, which are hydrolysed by mineral acids, giving NO and ethylnitrolic acid (Traube, Annalen, 300, 106).

Diethylamine $(C_2H_5)_2NH$; m.p. −40° (Hofmann, Ber. 22, 699); b.p. 57·5° (Hofmann, Annalen, 73, 91), 55·5° at 759 mm. (Oudemans, Rec. trav. chim. 1, 59); sp.gr. 0·7262 at 0°, 0·7107 at 15° (Hofmann, Ber. 22, 669), 0·7226 at 4°, 0·7116 at 15°, 0·7028 at 25°). From NH_3 and C_2H_5I (Hofmann), or NH_3 and $C_2H_5NO_3$ (Lea, J. 1861, 493). Prepared by the action of KOH upon the $C_2O_2N(C_2H_5)_2OC_2H_5$ obtained in manufacture of ethylamine (*q.v.*).

Also by action of very dilute NaOH solution upon $[(C_2H_5)_2N(NO)]_2H_2SO_4$ (Kopp, Ber. 8, 622). Also by action of EtOH upon phospham at 225°–250° (Vidal, D. R. P. 64346). By heating *p*-toluenesulphodiethylamide with chlorsulphonic acid at 130°–150° (Marckwald and v. Droste-Hülshoff, Ber. 31, 3263). By dissolving 50 grams diethylaniline in 148 grams HCl (sp.gr. 1·1), diluting with 75 c.c. H_2O, adding 32 grms. $NaNO_2$ in 50 c.c. H_2O and pouring slowly through a reflux condenser into a boiling solution of 85 grams NaOH in 2 litres of H_2O (Norris and Kimberley, Amer. Chem. J. 20, 60).

Is a colourless, inflammable liquid with strong ammoniacal smell, very soluble in water; is a strong base, and acts like $C_2H_5NH_2$, except that it does not dissolve $Zn(OH)_2$ (Carey Lea). H_2O_2 oxidises it to diethylhydroxylamine (Dunstan and Golding). The nitrate decomposes suddenly at 170°, and yields *nitrosodiethylamine* $(C_2H_5)_2NNO$ (Franchimont, Rec. trav. chim. 2, 95); the hydrochloride $(C_2H_5)_2NH,HCl$ forms non-deliquescent plates; m.p. 215°–217° (Wallach, Annalen, 214, 275); b.p. 320°–330° (W.); sp.gr. 1·0475 at 21°/4° (Schiff and Monsacchi); and combines with many metallic chlorides, *e.g.* $[(C_2H_5)_2NH,HCl]_2PtCl_4$, orange-yellow monoclinic crystals (Topsoë, J. 1883, 619).

Diethylchloramine $(C_2H_5)_2NCl$. A pungent-smelling oil; b.p. 91°; sp.gr. 0·943 at 0°; formed by action of NaClO upon $(C_2H_5)_2NH$. It decomposes on keeping with formation of $(C_2H_5)_2NH,HCl$ (Berg, Ann. Chim. Phys. [7] 3, 320).

Diethylnitramine $Et_2N{\cdot}NO_2$; b.p. 206·5° at 757 mm., 93° at 16 mm.; sp.gr. 1·057 at 15°. Formed by action of EtI upon $EtNK{\cdot}NO_2$; also by action of highest concentrated HNO_3 upon *as*-diethylurea. It is decomposed by KOH at 150°–160° into $EtNH_2$, HNO_2, and CH_3CHO (Franchimont, Rec. trav. chim. 6, 149; F. and Umbgrove, *ibid.* 16, 396).

Diethylisonitramine. An oil, b.p. 46°–50° at 18 mm.; sp.gr. 1·000 at 15°; formed by interaction of EtI and $C_2H_5NAgNO_2$. KOH at 100° decomposes it into alcohol, N, and CH_4CHO (U. and F. *l.c.* 399).

Nitrosodiethylamine $(C_2H_5)_2NNO$; b.p. 176·9° (corr.); sp.gr. 0·951 at 17·5°; V.D. = 3·36 (calc. = 3·53) (Knecht, Ber. 10, 979); by distilling neutral solution of $(C_2H_5)_2NH,HCl$ with a concentrated solution of KNO_2 (Geuther, Annalen, 128, 251; J. 1871, 695); also from $(C_2H_5)_2NH$ and NOCl in ether solution at −15° to −20° (Solonina, J. Russ. Phys. Chem. Soc. 30, 431); a yellow oil with aromatic smell, decomposed by HCl into $(C_2H_5)_2NH$ and HNO_2. Alcoholic KOH at 140° forms NH_3 and $(C_2H_5)NH_2$. Na amalgam forms N_2O and $(C_2H_5)_2NH$.

Triethylamine $(C_2H_5)_3N$; b.p. 89°–89·5° at 736·5 mm. (Brühl, Annalen, 200, 186), 89°–90·5° at 767·8 mm. (Hofmann); sp.gr. 0·735 at 15° (Hofmann, Ber. 22, 700), 0·7426 at 4°, 0·7331 at 15°, 0·7257 at 25° (Perkin); crit. temp. 267·1° (Pawlewski, Ber. 16, 2633); remains liquid at −75° under 10 mm. pressure (H.). By the action of NH_3 upon C_2H_5I (Hofmann, Annalen, 73, 91) or upon $C_2H_5NO_3$ (Carey Lea).

Preparation.—(1) Crude ethylamine (from C_2H_5Cl and NH_3) in alcoholic solution is treated with C_2H_5Cl (Duvillier and Buisine); (2) by distillation of $(C_2H_5)_4N{\cdot}OH$.

Properties.—An oily liquid with strong ammoniacal smell, slightly soluble in water; strong base. On strongly heating its salts, $(C_2H_5)_3N$ is destroyed, with formation of a little $(C_2H_5)_2N{\cdot}NO$ (Geuther, Zeitsch. Chem. 1886, 513).

The hydrochloride forms feathery non-deliquescent scales, and combines with many metallic salts to form double compounds. $N(C_2H_5)_3,HCl$, sp.gr. 1·06885 at 21°/4°. 1 part of water dissolves 1·5 parts salt (Schiff and Monsacchi). $(C_2H_5)_3N,HNO_3$, m.p. 98°–99° (Franchimont, Rec. trav. chim. 2, 339).

Tetra-ethylammonium hydroxide

$$(C_2H_5)_4N{\cdot}OH,$$

formed from the iodide $(C_2H_5)_4NI$ by the action of Ag_2O. It forms very deliquescent needles, is a strong base, which eagerly absorbs CO_2, displaces NH_3, precipitates metallic hydroxides, and gives a blue solution with sugar and $CuSO_4$; is decomposed by dry distillation, forming triethylamine, ethylene, and H_2O; when heated with C_2H_5I, gives $(C_2H_5)_4I$ and alcohol.

Salts.—$(C_2H_5)_4NCl$, forms deliquescent crystals, sp.gr. 1·0801 at 21°/4° (Schiff and Monsacchi); and yields many double salts, *e.g.* $[(C_2H_5)_4NCl]_2HgCl_2$, tetragonal crystals; $(C_2H_5)_4NCl,HgCl_2$, triclinic crystals (Topsoë, J. 1883, 620); $[(C_2H_5)_4NCl]_2PtCl_4$, orange-yellow, crystalline (monoclinic (T.)), difficultly soluble in water, almost insoluble in alcohol; $(C_2H_5)_4NBr$, light-orange needles, m.p. 78°, combines with Br to form an unstable pentabromide (Marquart, Ber. 3, 284); gives with alcoholic I solution a precipitate of $(C_2H_5)_4NI_3$, quadratic prisms (Weltzien, Annalen, 91, 33), which is also formed along with iodoform when the monoiodide is electrolysed between platinum electrodes (Goecke, Zeitsch. Elektrochem. 10, 249); the monoiodide $(C_2H_5)_4NI$ forms large crystals soluble in cold water and in alcohol, insoluble in ether; sp.gr. 1·559 (Schröder, Ber. 12, 562).

α-**Ethyl hydroxylamine** $C_2H_5O{\cdot}NH_2$; b.p. 65°; sp.gr. 0·8827 at 7·5° (Gürke, Annalen, 205, 277);

by the action of HCl upon benzoyl ethylhydroxylamine ethyl ether $C_6H_5CO{\cdot}NC_2H_5{\cdot}OC_2H_5$, or upon the ethyl ether of benzaldoxime

$$C_6H_5{\cdot}CH{:}NOC_2H_5$$

(Lossen and Zanni, *ibid.* 182, 223).

A strongly smelling inflammable liquid, miscible with water, alcohol, or ether; gives with $AgNO_3$ a white precipitate, which, on heating, is changed to metallic silver; with acids, forms salts, *e.g.* C_2H_7ON,HCl, scaly plates, m.p. 128°, decomposed by heating with HCl to 150° into C_2H_5Cl, NH_3O,HCl, and NH_4Cl; unites with $PtCl_4$ to form $(C_2H_7ON,HCl)_2PtCl_4$; prismatic crystals, soluble in water and in absolute alcohol (Lossen and Zanni). The sulphate $(C_2H_7ON)_2H_2SO_4$ crystallises with difficulty, and is soluble in water and in alcohol.

β-Ethyl hydroxylamine $C_2H_5NH{\cdot}OH$; m.p. 59°–60°, with decomposition; sp.gr. 0·9079 at 63·9° (Brühl). Formed by heating for 8 hours at 140°, β-ethyl-α-benzylhydroxylamine with conc. HCl (Behrend and Leuchs, Annalen, 257, 239); from hydroxylamine and EtI (Lobry de Bruyn, Rec. trav. chim. 13, 48; Hantzch and Hilland, Ber. 31, 2065; Dunstan and Golding, Chem. Soc. Trans. 75, 807); by heating 1 part *m*-nitrobenzsynaldoxime-N-ethyl ether with 7 parts conc. HCl (Kjellin, Ber. 26, 2378); by electrolytic reduction of nitroethane in H_2SO_4 solution at 15°–20° (Pierron, Bull. Soc. chim. [3] 21, 784).

It is very easily soluble in water or alcohol, less so in ether, benzene, or cold ligroin. It reduces Fehling's solution, and is reduced by HI to $C_2H_5NH_2$.

ββ-Diethyl hydroxylamine $(C_2H_5)_2N{\cdot}OH$; b.p. 130°–134°, with decomposition (Dunstan and Golding), b.p. at 15 mm. 47°–49° (Lachman); sp.gr. 0·8771 at 15°/15° (D. and G.), 0·8784 (L.). An oil formed by action of EtI upon NH_2OH, and also from $(C_2H_5)_2NH$ and H_2O_2 (D. and G. Chem. Soc. Trans. 75, 800). From addition product of diphenylnitrosamine and $Zn(Et)_2$ by decomposition with water, along with diphenylamine and $Zn(OH)_2$ (Lachman, Ber. 33, 1022).

Is a feeble base, soluble in water, alcohol, or ether. Reduces $AgNO_3$ and $HgCl_2$, and, on heating, $CuSO_4$. Reduced with HI, yields $(C_2H_5)_2NH$.

αβ-Diethyl hydroxylamine $C_2H_5NH{\cdot}OC_2H_5$; b.p. 83°; sp.gr. 0·829 at 0°; formed by interaction of α-ethylhydroxylamine and EtBr. It is easily soluble in water, alcohol, or ether. Heated with conc. HCl at 200°, yields $NH_2(C_2H_5)$ and C_2H_5Cl (Lossen, Annalen, 252, 230).

The hydrochloride $C_4H_{11}NOHCl$ of an isomeric compound is obtained by action of Sn and HCl upon $C_2H_5NO_3$ (Lossen, *ibid.* Suppl. 6, 238). The salts are more soluble in water than those of hydroxylamine. The free base is a syrup, easily soluble in water, and has strong basic properties. The platinum salt is in the form of orange-yellow plates, soluble in warm alcohol and in water.

Triethyloxamine $(C_2H_5)_3NO$ is a colourless crystalline mass obtained from ββ-diethylhydroxylamine and EtI. Also from NEt_3 and H_2O_2 (Dunstan and Golding; Lachman).

It is very easily soluble in water, less so in $CHCl_3$ and insoluble in ether. Decomposes on heating. Reduces Fehling's solution on heating. It gives a precipitate with $CuSO_4$ and $AgNO_3$. On reduction, yields triethylamine.

Triethyl methyl ammonium iodide

$$N(C_2H_5)_3CH_3I,$$

obtained by action of $N(C_2H_5)_3$ upon CH_3I (Hofmann, Annalen, 78, 277) (for other *Salts*, *v.* Topsoë, J. 1883, 620). The picrate melts at 267°–268° (Lossen, Annalen, 181, 374).

Diethyl dimethyl ammonium iodide, obtained from $N(CH_3)_2H$ and C_2H_5I; or from $N(C_2H_5)_2H$ and CH_3I (v. Meyer and Lecco, Annalen, 180, 177) (for other *Salts*, *v.* Topsoë, *l.c.*). The picrate melts at 285°–287° (Lossen, Annalen, 181, 374).

Ethyl trimethyl ammonium iodide is formed from $(CH_3)_3N$ and C_2H_5I (Müller, *ibid.* 108, 1) (for other *Salts*, *v.* Topsoë). The picrate melts at 299°–300° (Lossen).

Triethyl propyl ammonium iodide

$$N(C_2H_5)_3(C_3H_7)I$$

crystallises in large needles (Mendius, Annalen, 121, 136).

Diethyl *iso*amylamine $N(C_2H_5)_2(C_5H_{11})$; b.p. 154°; from the distillation of $N(C_2H_5)_3(C_5H_{11})OH$ (Hofmann); $[N(C_2H_5)_2C_5H_{11},HCl]_2PtCl_4$, yellow needles.

Triethyl *iso*amyl ammonium iodide

$$N(C_2H_5)_3(C_5H_{11})I,$$

formed by the action of $N(C_2H_5)_3$ upon $C_5H_{11}I$ (Hofmann, Chem. Soc. Trans. 1852, 4, 313; Annalen, 78, 279); the hydroxide decomposes on heating as follows:—

$$C_5H_{11}(C_2H_5)_3N{\cdot}OH = N(C_5H_{11})(C_2H_5)_2 + C_2H_4 + H_2O.$$

Diethyl methyl *iso*amyl ammonium iodide

$$N(C_2H_5)_2CH_3(C_5H_{11})I$$

is formed from $N(C_2H_5)_2(C_5H_{11})$ and CH_3I (Hofmann).

Ethyl-methyl-*iso*amylamine

$$NC_2H_5(CH_3)(C_5H_{11});$$

b.p. 135°; is obtained by distillation of the hydroxide of the radicle of the preceding compound (Hofmann).

Acetethylamide $CH_3{\cdot}CONHC_2H_5$; b.p. 205°, sp.gr. 0·942 at 4·5° (Wurtz); b.p. 204°–205° (Titherley); from ethyl acetate and ethylamine (Wurtz, Ann. Chim. Phys. [3] 30, 491; Compt. rend. 36, 180; Annalen, 76, 334) or from C_2H_5NCO and $HC_2H_3O_2$ (Wurtz, *ibid.* 88, 315); from $CH_3CONHNa$ and EtI at 150°. The hydrochloride forms deliquescent needles, melting at 60°. With $NaNH_2$, yields $CH_3CONNaC_2H_5$, which, with $KMeSO_4$, gives $CH_3CONMeEt$, an oil, boiling at 180°, and soluble in water (Titherley, Chem. Soc. Trans. 1901, 393). By action of Cl yields *ethyl acetyl nitrogen chloride* $NClEt(C_2H_3O)$ (Norton, Tcherniak, Bull. Soc. chim. [ii.] 30, 106; Compt. rend. 86, 1409), an oily unstable liquid, slightly soluble in water.

Acetdiethylamide $N(C_2H_5)_2C_2H_3O$; b.p. 185°–186°; sp.gr. 0·9248 at 8·5° (Wallach, Annalen, 214, 235).

Diacetylethylamide $NC_2H_5(C_2H_3O)_2$; b.p. 185°–192° (Wurtz); sp.gr. 1·0092 at 20° (W.); by heating EtNCO with $(C_2H_3O)_2O$ to 200° (Wurtz, Ann. Chim. Phys. [3] 42, 43).

Ethyl hydrazines-Ethylamide.

1. *Ethyl hydrazine* $C_2H_5HN{\cdot}NH_2$; b.p. 99·5° at 709 mm., is prepared by reducing nitrosodiethyl urea $N(C_2H_5)H{\cdot}CO{\cdot}N(NO)C_2H_5$

by means of zinc-dust and acetic acid; this yields ethyl hydrazine urea (semi-carbazide) $N(C_2H_5)H{\cdot}CO{\cdot}N(NH_2)C_2H_5$, and this, by action of HCl, forms $C_2H_5HN{\cdot}NH_2$, CO_2, and $C_2H_5NH_2$; by passing in HCl the chloride separates out, which is then decomposed by strong KOH solution and solid KOH, and the resulting oily liquid distilled over BaO (Fischer, Annalen, 199, 287); also by reducing ethylnitramine with Zn and HCl (Thiele and Meyer, Ber. 29, 963).

Is a colourless liquid, with faintly ammoniacal odour; has great affinity for water, in which it is soluble, as also in alcohol, ether, chloroform, and benzene; fumes in air and destroys cork and caoutchouc; reduces Fehling's solution in the cold. Br water liberates N. It precipitates metallic oxides, and gives the *iso*nitrile reaction with KOH and $CHCl_3$. Forms two chlorides: (1) $C_2H_8N_2,2HCl$, white needles, very soluble in water and alcohol; on heating to 110° yields (2) $C_2H_8N_2,HCl$, an amorphous horny deliquescent body. The sulphate crystallises from alcohol in thin plates, and is very soluble in water. By heating $C_2H_5NH{\cdot}NH_2$ with $K_2S_2O_7$ at 80°–100°, *potassium ethyl hydrazine sulphonate* $C_2H_5NH{\cdot}NHSO_3K$ is obtained; this forms fine needles, very soluble in water, much less soluble in alcohol or ether (Fischer).

2. *as-Diethylhydrazine* $(C_2H_5)_2N{\cdot}NH_2$; b.p. 96°–99°; prepared by action of zinc-dust and acetic acid upon a solution of nitrosodiethylamine $(C_2H_5)_2(NO)N$; 30 grams $(C_2H_5)_2(NO)N$ dissolved in 300 grams water are mixed with 150 grams Zn dust and 150 grams $C_2H_4O_2$ (of 50 p.c.) kept at 20°–30°, and, towards the end, at 40°–50°. Excess of Zn is then dissolved by HCl, an excess of NaOH added, and the mixture distilled; the distillate is neutralised with HCl and NH_4Cl separated by crystallisation. From the mother liquor $(C_2H_5)_2N_2H_2$ mixed with $(C_2H_5)_2HN$ is freed by solid KOH. By the action of HCNO diethylhydrazine urea (semicarbazide) $NH_2{\cdot}CO{\cdot}NH{\cdot}N(C_2H_5)_2$ is formed. 4 grams of this compound are heated with 15 grams of HCl in a sealed tube at 100°, diluted and the NH_4Cl separated; on treatment with KOH, pure $(C_2H_5)_2N_2H_2$ is obtained (Fischer, Annalen, 199, 308).

Is a colourless liquid with a faintly ammoniacal smell, very hygroscopic and soluble in water, alcohol, ether, chloroform, and benzene; reduces Fehling's solution only on warming; is monobasic; the salts are soluble in water and alcohol, and difficult to crystallise. $[(C_2H_5)_2N_2H_2{\cdot}HCl]_2PtCl_4$ forms fine yellow needles, soluble in water. With $SOCl_2$ in ice-cold ether, yields $(C_2H_5)_2N{\cdot}NSO$, an aromatic oil, b.p. 73° at 20 mm. It is slowly hydrolysed by water (Michaelis and Storbeck, Ber. 26, 310).

3. *sym-Diethylhydrazine* $C_2H_5{\cdot}HN{\cdot}NH{\cdot}C_2H_5$; b.p. at 758 mm. 84°–86°. Formed by heating at 100° for 3 hours 1 part *sym*-diethyl-diformylhydrazide and 2 parts fuming HCl; an oil; heated with conc. HCl. at 155°, yields NH_4Cl and C_2H_5Cl. With yellow HgO forms $HgEt_2$. With HNO_2 yields ethyl nitrite. The hydrochloride melts at 160° with decomposition (Harries, Ber. 27, 2279).

Triethyl-azonium iodide $(C_2H_5)_3NNH_2I$ is formed by action of diethylhydrazine upon $1\frac{1}{2}$ times its weight of C_2H_5I (Fischer, Annalen, 199, 316). It forms needles very soluble in water and in hot alcohol; insoluble in ether and strong alkalis. By action of Ag_2O, gives the strongly alkaline free base, which, on heating, yields $(C_2H_5)_2N{\cdot}NH_2$ and C_2H_4. By the action of nascent H (Zn and H_2SO_4), the iodide yields HI, NH_3, and $(C_2H_5)_3N$.

Tetra-ethyl tetrazone $(C_2H_5)_2N{\cdot}N{:}N{\cdot}N(C_2H_5)_2$; by the action of yellow HgO upon a cold aqueous solution of $(C_2H_5)_2N{\cdot}NH_2$ (Fischer, Annalen, 199, 319); is an oily liquid with a disagreeable smell, not volatile without decomposition, and which does not freeze at −20°. When decomposed by heat, yields N and $(C_2H_5)H_2N$. Forms an explosive oily compound with I. Is a strong base, though its salts are very unstable. It reduces silver solutions with formation of a mirror. The solution decomposes on heating, yielding N, $N(C_2H_5)_2H$, and aldehyde. The Pt double salt $[(C_2H_5)_4N_4,2HCl]_2PtCl_4$ forms yellow prisms soluble in water.

Ethylene C_2H_4, *Olefiant gas, Heavy carburetted hydrogen, Bicarburetted hydrogen, Elayl, Ethene, Etherin*, discovered by Deiman, Van Trootswyk, Bondt, and Lauwerenburgh (Crell's Ann. 1795, [2] 195, 310, 430). Obtained by action of H_2SO_4 upon alcohol; the addition of $Al_2(SO_4)_3$ increases the yield (Senderens, Compt. rend. 1910, 151, 392). The sulphuric acid can be replaced by syrupy phosphoric acid, sp.gr. 1·75 (Newth, Chem. Soc. Trans. 1901, 915); by the dry distillation of many organic bodies (hence occurs to the extent of 4 or 5 p.c. in coal gas). Also formed when CS_2 and H_2S (or PH_3) are led over heated copper (Berthelot, Annalen, 108, 194). To prepare the gas, a mixture of 25 parts (by weight) of alcohol and 150 parts sulphuric acid is heated to 170°, and a mixture of 1 part of alcohol and 2 of H_2SO_4 is allowed to drop slowly into the vessel by means of a funnel. The gas is passed through H_2SO_4,NaOH solution, and then again through H_2SO_4. For the preparation of small quantities of pure gas, an alcoholic solution of $C_2H_4Br_2$ is warmed with granulated Zn (Sabanejeff, J. Russ. Phys. Chem. Soc. 9, 33). Equal volumes of CO and H led over coke impregnated with reduced Ni and Pd heated at 95°–100°, yield 8·3 p.c. C_2H_4 (Orloff, *ibid.* 40, 1588).

Properties.—A colourless gas, liquefied by a pressure of $42\frac{1}{2}$ atmospheres at −1·1°; b.p. −105° (Cailletet, Compt. rend. 94, 1224), −102°–103° (Wroblewsky, Olszewsky, Monatsh. 4, 338); m.p. −169°, b.p. at 757 mm. −102·7°, sp.gr. 0·6095 at −102·7° (Ladenburg and Krugel, Ber. 32, 49, 1821); crit. temp. 13°; becomes liquid at 1° and 45 atmospheres, at 4° and 50 atmospheres, at 8° and 56 atmospheres, and at 10° and 60 atmospheres (C.); sp.gr. (air = 1) 0·9784. 1 volume of water absorbs at $t°$, $0{\cdot}25629-0{\cdot}009136t+0{\cdot}0001881t^2$ volumes C_2H_4 (Bunsen). Alcohol (of sp.gr. 0·792 at 20°) absorbs $3{\cdot}59498-0{\cdot}05772t+0{\cdot}000681t^2$ volumes (Carius, Annalen, 94, 133); H.C.p. =341·4 Cals.; H.F. (from amorphous C) = −9·4 Cals. (Berthelot, Ann. Chim. Phys. [5] 23, 180).

Ethylene forms an explosive mixture with oxygen, and explodes, even in the cold, in contact with ozonised oxygen (Houzeau and Renard, J. 1873, 319). Led through a hot tube, it splits up into C, H, CH_4, C_2H_6, and C_2H_2 (Berthelot, Annalen, 139, 277; Bone and Coward, Chem. Soc. Trans. 1908, 1197). Decomposed by leading over reduced Ni at 300° into C, C_2H_6,

CH_4, and H (Sabatier and Senderens, Compt. rend. 124, 616, 1358). By the action of the electric spark it forms C_2H_2 and H, and then C and H (Wilde, Zeitsch. Chem. 1866, 735). It combines with H to form C_2H_6, when the mixture is passed through a hot tube (Ann. Chim. Phys. [4] 9, 431; Bull. Soc. chim. [ii.] 39, 145), or when in contact with Pt black in the cold (Wilde, Ber. 7, 354). By heating a mixture of C_2H_4 and CO_2 at 400°, aldehyde is formed (Schützenberger, Bull. Soc. chim. [ii.] 31, 482). CrO_3 converts it into aldehyde at 120° (Annalen, 150, 373). Fuming sulphuric acid absorbs readily large quantities of C_2H_4 at ordinary temperatures, as does also common H_2SO_4 at 160°–170° (Butlerow, Ber. 6, 193), forming $C_2H_5HSO_4$ (Faraday). C_2H_4 combines at 100° with strong HI or HBr solution, but not with HCl (Berthelot, Annalen, 104, 184; 115, 114). N_2O_4 reacts with ethylene to form ethylene nitrosite, and N_2O_5 to form ethylene nitrate (Demjanow, Chem. Zentr. 1899, i. 1064). In presence of $AlBr_3$, HBr unites at 0° with C_2H_4, forming C_2H_5Br. With Cl_2O, *chlorethyl chloracetate* $CH_2Cl{\cdot}CO_2C_2H_4Cl$ is formed, whilst ClO_2 yields $CH_2Cl{\cdot}CO_2H$. C_2H_4 combines with BF_3 in sunlight to form $C_2H_3BF_2$ (Landolph, Ber. 12, 1586), a liquid, b.p. 124°–125°, sp.gr. 1·0478 at 23°. Ethylene acts as a divalent radicle, and forms salts with most of the acids.

Ethylene acetates (Wurtz, Compt. rend. 43, 199; Atkinson, Phil. Mag. [4] 16, 433).

1. *Ethylene monoacetate* $C_2H_4(C_2H_3O_2)OH$, *monoacetic glycol*; b.p. 190°–190·5° (corr.) (Perkin, Chem. Soc. Trans. 45, 505); sp.gr. 1·1108 at 15°/15°, 1·1018 at 25°/25° (P.); produced by action of $KC_2H_3O_2$ upon $C_2H_4Br_2$ in presence of alcohol (Atkinson, *l.c.*; *cf.* Seelig, D. R. P. 41507). A liquid not miscible with water; yields glycol $C_2H_4(OH)_2$ by heating with $C_2H_4Br_2$ and alcohol (Demole, Annalen, 177, 45); decomposed by heating with C_2H_3OCl into acetochlorhydrin and ethylene diacetate (Lourenço, *ibid.* 114, 127).

2. *Ethylene diacetate* $C_2H_4(C_2H_3O_2)_2$; b.p. 186°–187°; sp.gr. 1·128 at 0°; prepared from $C_2H_4Br_2$ or $C_2H_4I_2$ and $AgC_2H_3O_2$ (Wurtz, Ann. Chim. Phys. [3] 55, 433), or from $C_2H_4Br_2$ and anhydrous $KC_2H_3O_2$ at 150°–200° (Demole).

A liquid soluble in 7 parts of water, isomeric with *ethylidene diacetate* $CH_3{\cdot}CH(C_2H_3O_2)_2$; b.p. 108·8°; sp.gr. 1·061 at 12°; prepared from aldehyde and $(C_2H_3O)_2O$. *Dichlorethylene diacetate* $C_2H_2Cl_2(C_2H_3O_2)_2$; b.p. 120° at 20 mm.; is produced by action of chloracetic acid upon C_2H_2 (Prudhomme, Zeitsch. Chem. 1870, 397).

Ethylene acetochlorhydrin

$$ClCH_2{\cdot}CH_2{\cdot}O{\cdot}C_2H_3O;$$

b.p. 145°; sp.gr. 1·1783 at 0°; by heating a mixture of glycol and acetic acid at 100° with HCl (Simpson, Annalen, 112, 147); from C_2H_4 and $CH_2Cl{\cdot}CO_2H$ (Schützenberger and Lippman, *ibid.* 138, 325); insoluble in water; yields ethylene oxide by action of KOH.

Ethylene acetoiodohydrin $ICH_2{\cdot}CH_2{\cdot}O{\cdot}C_2H_3O$, heavy oil; and

Ethylene acetobromohydrin

$$BrCH_2{\cdot}CH_2{\cdot}O{\cdot}C_2H_3O;$$

b.p. 161°–163°; are prepared from

$$C_2H_4(C_2H_3O_2)OH$$

by action of HI and HBr respectively, the former in the cold in presence of $C_2H_4(OH)_2$ and $CH_3{\cdot}CO_2H$ (Simpson, Annalen, 113, 123), the latter at 100° (Demole, *ibid.* 173, 120).

Ethylene glycols.

1. **Ethylene glycol** $CH_2OH{\cdot}CH_2OH$; *glycol*; m.p. −17·4°; b.p. 197·37° (Ladenburg and Krugel, Ber. 32, 1821); b.p. 197°–197·5° at 764·5 mm. (Wurtz), 196°–199° (corr.) (Perkin, Chem. Soc. Trans. 45, 504), 195° at 751·3 mm. (Přibram and Handl, Monatsh. 2, 673); sp.gr. 1·125 at 0° (W.), 1·1279 at 0° (P. and H.), 1·1168 at 15°/15°, 1·112 at 25°/25° (Perkin).

Discovered by Wurtz (Compt. rend. 43, 199; Ann. Chim. Phys. [3] 55, 400). Formed by action of ethylene diacetate upon KOH (W.); from C_2H_4ClI and moist silver oxide at 160°–200° (Simpson, Annalen, Suppl. 6, 253); by heating ethylene monacetate with $Ba(OH)_2$ or with water in sealed tubes (Debus, Annalen, 110, 316); by heating a strong aqueous solution of neurine, when glycol and $N(CH_3)_3$ are formed (Wurtz, *ibid.* Suppl. 6, 200); by heating ethylene chloride or bromide with PbO and 15–20 times its volume of water at 140°–170° (Eltekow, Ber. 6, 558); from ethylene bromide and water at 140°–150° (Niederist, Annalen, 186, 393); together with polyethylene glycol, by action of C_2H_4O (oxide of ethylene) upon water in sealed tubes (Wurtz, *ibid.* 113, 255).

Preparation.—1. 600 grams ethylene bromide, 700 grams fused potassium acetate, and 1500 grams alcohol (sp.gr. 0·83) are heated in a flask with reflux condenser until all action ceases; cooled, filtered from KBr and filtrate distilled; the portion distilled above 140° is decomposed by slight excess of $Ba(OH)_2$ and heated for 12 hours on water-bath. The excess of baryta is removed by CO_2, the liquid evaporated to one-third its volume, the residue treated with a mixture of alcohol and ether, the liquid removed from the crystals and distilled, first on water-bath, to separate alcohol and ether, and then over the flame; the portion distilling above 185° is then redistilled (Erlenmeyer, Annalen, 192, 244).

2. A mixture of 188 grams ethylene bromide, 138 grams potassium carbonate and 1 litre of water [or 32 parts $C_2H_4Br_2$, 25 parts K_2CO_3, 350 parts H_2O (Groscheintz, Bull. Soc. chim. [ii.] 31, 293)], is heated with reflux condenser for 10 hours, is then evaporated to small volume on water-bath, the liquid portion poured off the crystals of KBr, the latter are washed with absolute alcohol. The filtrate and alcoholic washings are then distilled as in previous method; a loss owing to formation of C_2H_3Br is experienced by this process (Zeller and Hüffner, J. pr. Chem. [2] 11, 229). Haworth and Perkin (Chem. Soc. Trans. 1896, 175) obtained a 60 p.c. yield by digesting 138 grams K_2CO_3 in 1000 c.c. H_2O with 188 grams $C_2H_4Br_2$ under a reflux condenser. The solution is evaporated very slowly to a syrup, and then extracted with a mixture of alcohol and ether.

3. 1 part of ethylene bromide and 26 parts water are heated to 100° in a sealed vessel for 130 hours. This method gives a yield of over 60 p.c. of the theoretical amount (Niederist, Annalen, 196, 354).

4. Glycol diacetate is decomposed with powdered $Ca(OH)_2$, and the mixture distilled under reduced pressure. The yield of glycol is 93 p.c. of theory (Henry, Rec. trav. chim. 18, 221).

5. It may also be prepared by heating ethylene diacetate with methyl alcohol and hydrochloric acid (Henry, Bull. Acad. Roy. Belg. 1896, 732).

Glycol is a colourless, odourless, syrupy liquid with sweet taste, miscible with alcohol and water, but almost insoluble in ether. 100 parts ether dissolve 1·1 part of glycol (Knorr, Ber. 30, 912). It dissolves NaCl, $ZnCl_2$, and many other chlorides; also K_2CO_3, KOH, and $Ca(OH)_2$.

By action of oxidising agents, *e.g.* platinum black, it forms glycollic acid. Nitric acid converts it into glycollic acid, glyoxylic acid, and oxalic acid (Debus, Annalen, 110, 316). Heated with solid KOH to 250°, glycol yields potassium oxalate and hydrogen (Wurtz). Heated with large quantity of water at 200°–210° yields aldehyde (Nevole, Bull. Soc. chim. [ii.] 25, 289); $ZnCl_2$ at 250° decomposes glycol into aldehyde, crotonaldehyde, and water. By electrolysis of an acid (H_2SO_4), solution of glycol, formic acid, formaldehyde, CO_2, traces of a sugar and a non-volatile acid, not glycollic, are formed. (Löb and Pulvermacher, Zeitsch. Elektrochem. 1910, 16, 1). Chlorine forms a crystallisable halogen compound, m.p. 39°, b.p. 200°; and an oily body, $C_8H_{12}O_4$, b.p. 240° (Mitscherlich, J. 1863, 485). H_2O_2 in presence of ferrous compounds yields glycollic aldehyde (Fenton and Jackson, Chem. Soc. Trans. 1899, 75). Heated with aldehydes, glycol yields ethylene oxide derivatives, *e.g.* glycol and œnanthaldehyde heated at 125°–130° for some days yield ethylene œnanthylidene oxide

$$C_6H_{13}\cdot CH\langle\begin{matrix}OCH_2\\OCH_2\end{matrix}\rangle,$$

b.p. 180°; similarly, valeraldehyde and propaldehyde yield $C_4H_9\cdot CH\langle\begin{matrix}OCH_2\\OCH_2\end{matrix}\rangle$, b.p. 142°; and $C_2H_5\cdot CH\langle\begin{matrix}OCH_2\\OCH_2\end{matrix}\rangle$, b.p. 105°–107°, respectively (Lochert, Bull. Soc. chim. [ii.] 48, 337, 716). With Na and EtI, yields glycol monoethyl ether, a liquid boiling under 748 mm. at 134·8°, and having a density of 0·93535 at 15°/15° (Palomaa, Ber. 42, 3873).

Glycol is converted into glycollic acid by the action of *Bacterium aceti*, provided the acid be neutralised (*e.g.* by $CaCO_3$) as fast as formed, otherwise after a short time the glycollic acid formed stops the further action (A. J. Brown, Chem. Soc. Trans. 51, 638). NH_4Cl and glycol at 300°–400° form *collidine*, $C_8H_{11}N\cdot HCl$ (Hofmann, Ber. 17, 1905). Phosgene gas at ordinary temperatures converts glycol into *glycol carbonate* $CO(OCH_2)_2$ (with liberation of HCl), a stable compound, soluble in water, alcohol, and ether, and crystallising in colourless needles (Nemirowsky, J. pr. Chem. [2] 28, 439). Heated with strong formic acid for some time (Henninger, Ber. 7, 263), or with oxalic acid (Lorin, Bull. Soc. chim. [ii.] 22, 104), gives *glycol diformin* $C_2H_4(CH_2O)_2$, b.p. 174°; in the latter case formic acid is also produced. With mineral acid or dehydrating agents yields acetaldehyde, ethylidene ethylene ether and chiefly diethylene ether

$$O\langle\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}\rangle O$$

(Faworsky, J. Russ. Phys. Chem. Soc. 1906, 38, 741). By action of sodium on glycol, we get *sodium ethylenate* $C_2H_4(OH)ONa$, a white crystalline deliquescent body, which, on heating to 190° with more sodium yields *disodium ethylenate*, a deliquescent mass. The former, with C_2H_3Br in a sealed tube, yields ethylene, glycol, NaBr, and probably $NaCHO_2$ (Wurtz).

De Coninck (Bull. Acad. Roy. Belg. 1905, 360) distinguishes between glycol and glycerol as follows. Uranyl sulphate is dissolved in a small quantity of water, excess of ethylene glycol added, the whole placed in a flask and exposed to sunlight. In 2 hours the liquid is quite green, and in 2½ hours uranous sulphate is precipitated. With glycerol no such colouration or precipitation takes place.

Glycol forms a number of cyclic esters and cyclic compounds analogous to the metallic saccharates (Bischoff, Ber. 40, 2803; Grün and Bockisch, *ibid.* 41, 3465).

2. Diethylene glycol

$$HO\cdot CH_2\cdot CH_2\cdot O\cdot CH_2\cdot CH_2\cdot OH;$$

b.p. 250°, sp.gr. 1·132 at 0°; V.D. = 3·78 at 311° (calc. 3·67) (Lourenço, Ann. Chim. Phys. [3] 67, 275); from ethylene oxide and water, or better, ethylene oxide and glycol at 100° (Wurtz); from glycol and ethylene bromide or bromhydrin at 115°–120° (Lourenço); by action of glycol monoacetate upon sodium glycol at 130°–140° (Mohs, Zeitsch. Chem. 1866, 495).

An oily liquid, soluble in water, alcohol, and ether; concentrated HI at 100° forms $C_2H_4I_2$; oxidised by HNO_3 to glycollic acid, oxalic acid, and diglycollic acid $C_4H_6O_5$. The *chlorhydrin* $C_4H_9O_2Cl$, b.p. 180°–185° (L.), 190°–200° (W.), is formed by leading HCl into ethylene oxide, or from ethylene oxide and ethylene chlorhydrin at 140° (Wurtz, Ann. Chim. Phys. [3] 69, 338). 1 molecule ethylene chlorhydrin and 2 molecules glycol are heated at 140°, saturated with HCl and again heated at 100° (Lourenço, *ibid.* [3] 67, 290); a liquid soluble in water.

The *bromhydrin*, b.p. 205°, is prepared from glycol and ethylene bromide at 160° (L.).

3. Tri-ethylene glycol

$$C_2H_4(OH)\cdot O\cdot C_2H_4\cdot O\cdot C_2H_4OH;$$

b.p. 290°; sp.gr. 1·138; a liquid miscible with alcohol and water, and oxidised by HNO_3 to *diglycol-ethylenic acid* $C_6H_{10}O_6$ (Lourenço; Wurtz).

The *chlorhydrin* $C_6H_{13}O_3Cl$; b.p. 222°–232°; is a liquid soluble in water (L.).

The *bromhydrin* $C_6H_{13}O_3Br$; b.p. (with decomposition) 250° (L.).

4. Tetra-ethylene glycol $C_8H_{18}O_5$; b.p. 230°; at 25 mm. (L.; W.).

The *chlorhydrin* $C_8H_{17}O_4Cl$; b.p. 262°–272°, is soluble in water (L.).

5. Penta-ethylene glycol $C_{10}H_{22}O_6$; b.p. 281° at 25 mm.; a viscid liquid soluble in water, alcohol, and ether (L.).

6. Hexa-ethylene glycol $C_{12}H_{26}O_7$; b.p. 325° at 25 mm.; a very viscid liquid (L.).

Ethylene bromide $C_2H_4Br_2$ or $CH_2Br\cdot CH_2Br$; m.p. 9·53° (Regnault, Ann. Chim. Phys. [2] 59, 358); b.p. 131·6° (R.), 129·5° at 745 mm. (Anschütz, Annalen, 221, 137); sp.gr. 2·1827

at 20° (Haagen, Bull. Soc. chim. [ii.] 10, 355), 2·2132 at 0°/4°, 2·1901 at 10·9°/4° (Thorpe, Chem. Soc. Trans. 37, 177); by actien of C_2H_4 and Br (Balard, Ann. Chim. Phys. [2] 32, 375); formed together with ethylidene bromide CH_3CHBr_2 by heating C_2H_5Br with Br to 180° (Tawildarow, Annalen, 176, 14). From C_2H_5Cl, Br, and iron wire at 100° (V. Meyer and Petrenkò, Ber. 25, 3307); also from C_2H_2Br, Br, and $AlBr_3$ at 65°–70° (Mouneyrat, Bull. Soc. chim. [iii.] 19, 497).

Preparation.—1. Ethylene, purified by passing through H_2SO_4 and NaOH solution, is led into bromine covered with water, contained in a wide tube, until the colour of the Br disappears; the product is washed with NaOH and water, dried by $CaCl_2$ and distilled (Erlenmeyer and Bunte, Annalen, 168, 64; Erlenmeyer, *ibid.* 192, 244). 2. By heating together at 150° in glacial acetic acid glycol diacetate and HBr, a quantitative yield of $C_2H_4Br_2$ is obtained (Perkin and Simonsen, Chem. Soc. Trans. 1905, 856).

Is a colourless mobile liquid with a pleasant smell and sweet taste; V.D. 6·485 (Regnault). When heated with water to 150°–160°, it yields, first glycol, and, on longer heating, HBr and aldehyde (Carius, Annalen, 131, 173). Zn acts upon an alcoholic solution of $C_2H_4Br_2$ with formation of C_2H_4 and $ZnBr_2$ (Gladstone, Ber. 7, 364); by heating with KI and water, ethane is produced. Alcoholic KOH yields C_2H_3Br, and in excess C_2H_2. Heated with $AlBr_3$ at 100°–110°, yields C_2H_2 and $C_2H_2Br_4$; with Cl and $AlCl_3$, yields C_2Cl_4 (Mouneyrat).

Aqueous KOH produces, after long contact, C_2H_3Br (Stempnevsky, Annalen, 192, 240). By heating with strong NaOH or KOH solution, glycol and C_2H_3Br are produced. If $C_2H_4Br_2$ be heated with excess of H_2O and PbO to 220°, aldehyde is formed (due to decomposition of $C_2H_4(OH)_2$, first formed, into C_2H_4O and H_2O) (Eltekow, Ber. 6, 558, and Nevole, *ibid.* 9, 447). Heated with strong HI solution, yields $C_2H_4I_2$ (Sororkin, Zeitsch. Chem. 1870, 519). Heated with Ag_2O and water, aldehyde is produced, and when heated with Ag_2CO_3 and water, yields glycol (Beilstein and Wiegand, Ber. 15, 1368). Treated with Ag_2SO_4 and benzene, yields dibromethyl sulphate $(C_2H_4Br)_2SO_4$; with Ag_2SO_4 and water, bromethyl sulphuric acid $(C_2H_4Br)HSO_4$ (B. and W.).

Bromethylene bromide $CH_2Br{\cdot}CHBr_2$; b.p. 186·5° (Wurtz, Annalen, 104, 243); 187°–188° at 721 mm. (Denzel, *ibid.* 195, 202), 191° (Tawildarow, *ibid.* 176, 22), 73° at 11·5 mm., 83° at 18 mm., 187°–188° at 751·5 mm. (Anschütz, *ibid.* 221, 138); sp.gr. 2·624 at 16° (T.), 2·620 at 23° (W.), 2·6189 at 17·5°/4°, 2·6107 at 21·5°/4° (A.).

Prepared from monobromethylene and Br (Wurtz); from C_2H_3I and Br (Simpson, J. 1857, 461); from C_2H_3Br and Br at 170° (Hofmann, J. 1860, 364); or from $C_2H_4Br_2$ and Br at 200° (Tawildarow); decomposed by $KC_2H_3O_2$ at 150°, or by H_2O and PbO into dibromethylene and HBr. C_2H_5NaO yields ethylidene dibromide (Gray, Chem. Soc. Trans. 1897, 1024). Alcoholic KOH gives $C_2H_2Br_2$, C_2H_2, and bromacetylene C_2HBr. When heated with excess of absolute alcohol, C_2H_3Br and probably C_2H_3BrO bromaldehyde, are formed (Glöckner, Annalen, Suppl. 7, 110).

The isomeric body CH_3CBr_3 is not known.

Dibromethylene dibromide $C_2H_2Br_4$. Two isomerides are known.

1. *Acetylidine tetrabromide*; $CH_2Br{\cdot}CBr_3$ boils with decomposition at 200°; b.p. 103·5° at 13·5 mm.; sp.gr. 2·9292 at 17·5°/4°, 2·9216 at 21·5°/4° (Anschütz, Annalen, 221, 140). Formed from *as*-dibromethylene $CH_2:CBr_2$ and bromine (Lennox, *ibid.* 122, 124; Chem. Soc. Trans. 1862, 206; Reboul, Annalen, 124, 270). From C_2H_5Br and Br at 180° a compound $C_2H_2Br_4$ is produced, which boils with decomposition at 208°–211° (Tawildarow). By heating a mixture of pyrotartaric acid and bromine with water at 150° (Bourgoin, Ann. Chim. Phys. [5] 12, 427).

2. *Acetylene tetrabromide* $CHBr_2CHBr_2$; b.p. 137°–137·2° at 36 mm., 114° at 12 mm., at 15 mm. 124°–126°, at 54 mm. 151°; sp.gr. 2·9710 at 17·5°/4°, 2·9629 at 21·5°/4° (Anschütz, Ber. 12, 2974, and Annalen, 221, 139); decomposes at 190° into HBr, Br, and C_2HBr_3.

By leading C_2H_2 into bromine covered with water (Reboul, Annalen, 124, 269; Berthelot, Bull. Soc. chim. [ii.] 5, 97); the crude $C_2H_2Br_4$ is then reduced by means of alcohol and Zn dust to $C_2H_2Br_2$, when the admixed $C_2H_2Br{\cdot}Br_2$ is converted into C_2H_3Br; the $C_2H_2Br_2$ is then purified by distillation and treated with bromine (Anschütz, Annalen, 221, 139); by action of Br and $AlBr_3$ at 105°–110° upon $C_2H_4Br_2$ (Mouneyrat, Bull. Soc. chim. [iii.] 19, 498). A liquid smelling of camphor and chloroform; decomposed by heating or by action of Na; by heating with alcoholic KOH, C_2H_2 and C_2HBr are produced. Cl produces $C_2Cl_4Br_2$ (Bourgoin, Bull. Soc. chim. [ii.] 23, 4); when heated with Br and water to 180°, yields C_2Br_4 and C_2Br_6 (Anschütz); with C_6H_6 and $AlCl_3$, produces anthracene; heated with aniline, dimethylaniline, or alcoholic NH_3, yields $CHBr:CBr_2$.

Pentabromethane $CHBr_2{\cdot}CBr_3$; m.p. 56°–57° (Bourgoin), 54° (Denzel, Ber. 12, 2208), 48°–50° (Reboul); boils with decomposition at 210° (at 300 mm.) (Denzel). From C_2HBr_3 (Elbs and Newmann, J. pr. Chem. [2] 58, 254; Lennox, Annalen, 122, 125) or C_2HBr (Reboul, *ibid.* 124, 268) and bromine. By slow oxidation (by exposure to air) of C_2HBr_3 (Demole, Bull. Soc. chim. [ii.] 34, 204); from $C_2H_2Br_4$ and Br at 165° (Bourgoin, *ibid.* 23, 173). Forms prismatic needles soluble in alcohol and ether.

Perbromethane C_2Br_6 *v.* CARBON TRIBROMIDE

Ethylene bromoiodide; m.p. 28°; b.p. 163°; sp.gr. 2·516 at 29°. From C_2H_3Br and conc. HI at 100° (Reboul, Annalen, 155, 213). From C_2H_4 and IBr (Simpson, J. 1874, 326). Needles, with alcoholic KOH yields, in the cold, C_2H_3I and HBr, and on warming HBr, HI, and C_2H_2. Forms iodoform with alcoholic CH_3COOK at 100°.

Ethylene bromhydrin $C_2H_4Br{\cdot}OH$, *Glycol bromhydrin*; b.p. 150°–152°, at 18 mm. 63°–64° (Henry, J. 1889, 1321), 155° (Lourenço, Ann. Chim. Phys. [3] 67, 287); sp.gr. 1·66 at 8° (H.); sp.gr. 1·7195 at 18·6° (H.). From glycol and $C_2H_4Br_2$ at 115°–120° (Lourenço); from glycol and HBr at 100°, and from $CH_2I{\cdot}CH_2OH$ and bromine (Henry); also from 3 mols. glycol and 1 mol. PBr_5 (Demole, Ber. 9, 48); from ethylene and HBrO (60 p.c.) (Mokiewsky, J.

Russ. Phys. Chem. Soc.. 30, 900); with zinc-dust and alcohol is reduced to C_2H_4.

Ethylene dichloride, *Elayl chloride*, *Dutch liquid* CH_2ClCH_2Cl; b.p. 84·9° (Pierre, J. 1847–48, 63), 83·5° (corr.) (Thorpe, Chem. Soc. Trans. 37, 182), 84·5°–85° at 750·9 mm. (Brühl, Annalen, 203, 10), 83·3° at 749 mm. (R. Schiff, *ibid.* 220, 96), 84·1° at 760 mm. (Städel, Ber. 15, 2563); sp.gr. 1·2808 at 0°/4° (Thorpe), 1·2803 at 0° (Pierre), 1·2562 at 20° (Haagen, Bull. Soc. chim. ii. 10, 355), 1·2656 at 9·8°/4°, 1·1576 at 83·3°/4° (R. Schiff), 1·2606 at 14·4°, 1·204 at 62·5° (Landolt and John); refractive index at $t°$ $\mu_A = 1{\cdot}441466 - 0{\cdot}000446t$, mol. refract. = 34·06 (Kanonnikow); capill. constant at b.p. $a^2 = 4{\cdot}198$ (R. Schiff, Annalen, 223, 72). By action of C_2H_4 upon Cl (Deiman, Troostwyk, Bondt, and Lauwerenburgh, Crell's Ann. 1795, 2, 200); by leading C_2H_4 into $SbCl_5$ or into molten $CuCl_2$ (Wöhler, Pogg. Ann. 13, 297); from C_2H_5Cl and $SbCl_5$ at 100° (V. Meyer and Müller, J. pr. Chem. [ii.] 46, 173); also by action of glycol upon PCl_3 (Wurtz) or upon HCl at 100° (Schorlemmer, Chem. Soc. Trans. 1881, 1); from ethylene diamine and NOCl in carefully cooled *m*-xylene solution (Solonina, J. Russ. Phys. Chem. Soc. 30, 606). Prepared best according to Limpricht's method (Annalen, 94, 245). Ethylene is passed into a gently heated mixture of 2 parts manganese dioxide, 3 parts common salt, 4 parts water, and 5 parts sulphuric acid, and when the mass turns yellow it is distilled. It forms an oily liquid, insoluble in water. When heated with alcoholic KOH, it yields KCl and C_2H_3Cl, and with K it forms H, KCl, and C_2H_3Cl (Liebig, Annalen, 14, 37). Heated with $AlCl_3$ to 80°–85° is decomposed into HCl and C_2H_2 (Mouneyrat, Bull. Soc. chim. [iii.] 19, 446). With NH_3 it forms bases, $N_2H_4C_2H_4$, $N_2H_2(C_2H_4)_2$, &c. With ethylamine, it yields *collidine* (*trimethylpyridine* $C_5H_2(CH_3)_3N$), C_2H_5Cl, and also NH_3 and $N(C_2H_5)_3$ (Hofmann, Ber. 17, 1907).

Chlorethylene $CH_2:CHCl$, *Vinyl chloride*; at ordinary temp. a gas; b.p. −18° to −15°; by action of alcoholic KOH upon ethylene chloride (Regnault, Annalen, 14, 28), or ethylidene chloride (Wurtz and Frapolli, *ibid.* 108, 224). To prepare it the ethylene dichloride and alcoholic potash are left in contact for 3 or 4 days in the cold, and the mixture is then warmed. Combines with Cl to form $C_2H_3Cl_3$. Polymerises in sunlight, and forms a solid insoluble mass of sp.gr. 1·406 (Baumann, Annalen, 163, 317).

Dichlorethylene $C_2H_2Cl_2$.

1. *Dichlorethylene* $CH_2:CCl_2$; b.p. 33·5°–35° (Jocitsch and Faworsky); b.p. 37° (Kramer, Ber. 3, 261); sp.gr. 1·250 at 15°, obtained by action of alcoholic KOH upon $CH_2Cl{\cdot}CHCl_2$ (Regnault, J. pr. Chem. [ii.] 18, 80). Also by action of Zn shavings in alcoholic solution upon the trichlorethyl ester of acetic acid (Jocitsch and Faworsky, J. Russ. Phys. Chem. Soc. 30, 998). Polymerises easily into a solid amorphous insoluble body.

2. *Sym-Dichlorethylene* (*Acetylene dichloride*) $CHCl:CHCl$; b.p. 55°; by distillation of the compound of C_2H_2 with $SbCl_5$ (Berthelot and Jungfleisch, Annalen, Suppl. 7, 253); also by action of Zn upon an alcoholic solution of $CHClBr{\cdot}CHClBr$, or by leading C_2H_2 into aqueous solution of ICl (Sabanejeff, Annalen, 216, 262).

Trichlorethylene $CHCl:CCl_2$; b.p. 87·4°–87·55°; sp.gr. 1·4904 at 4°/4°, 1·4598 at 25·5°/25·5° (Valey, Proc. Roy. Soc. 1910, B 82, 217). From isomeric compounds $C_2H_2Cl_4$, and alcoholic KOH (Berthelot and Jungfleisch); also by action of nascent H (Zn and H_2SO_4) upon C_2Cl_6 (Fischer, J. 1864, 481); from anhydrous chloral and P_2S_5 at 160°–170° (Paternò and Oglialoro, Ber. 7, 81); combines with Cl to form C_2HCl_5.

Tetra-chlorethylene C_2Cl_4 *v. Carbon dichloride*, art. CARBON.

Hexachlorethane C_2Cl_6 *v. Carbon trichloride*, art. CARBON.

Ethylene chlorhydrin $HO{\cdot}CH_2{\cdot}CH_2Cl$. *Chlorethyl alcohol*, *Glycol chlorhydrin*; b.p. 128° (Wurtz, Annalen, 110, 125), 132°, 51°–52° at 22 mm.; sp.gr. 1·2005 at 18·6° (Henry, J. 1889, 1321), 1·24 at 8°. From glycol and HCl (gas) at 100° (W.). If excess of HCl be used, $C_2H_4Cl_2$ is produced (Schorlemmer, Chem. Soc. Trans. 39, 143); from glycol and Cl_2S_2 (Carius, Annalen, 124, 257); from C_2H_4 and ClOH (Carius, *ibid.* 126, 197; Butlerow, *ibid.* 144, 40). Dry HCl is led into glycol kept at 148°; the $C_2H_4Cl(OH)$ distils off (Ladenburg, Ber. 16, 1408). A liquid miscible with water; yields alcohol with Na amalgam and H_2O (Lourenço, Annalen, 120, 92). Oxidised by CrO_3 to chloracetic acid (Kriwaxin, Zeitsch. Chem. 1871, 265); with KOH, yields ethylene oxide.

Ethylene chlorobromide $CH_2Cl{\cdot}CH_2Br$; b.p. 107°–108° (Lescœur, Bull. Soc. chim. [ii.] 29, 484); sp.gr. 1·79 at 0° (L.), 1·705 at 11° (Montgolfier and Giraud, *ibid.* 33, 12), 1·689 at 19°. By action of Br upon $CH_2Cl{\cdot}CH_2I$ (Henry, Annalen, 156, 14); from $C_2H_4Br_2$ and $SbCl_5$ (Lössner, J. pr. Chem. [2] 13, 421) or $C_2H_4Br_2$ and $HgCl_2$ at 150°–180° (M. and G.); by action of Br upon $C_2H_4Cl(OH)$ at 130° (Demole, Ber. 9, 556). To prepare it, first chlorine and then ethylene is passed into Br, kept under a mixture of equal vols. of strong HCl and water (James, J. pr. Chem. [2] 26, 380; also Simpson, Proc. Roy. Soc. 27, 118); decomposed by alcoholic KOH, with formation of C_2H_3Cl.

Ethylene chloriodide $CH_2Cl{\cdot}CH_2I$; m.p. −15·6° (Schneider, Zeitsch. physikal. Chem. 19, 157), b.p. 140° (Sorokin, Zeitsch. Chem. 1870, 519), 140·1° (corr.) (Thorpe, Chem. Soc. Trans. 37, 189), 137°–138° (Meyer and Wurster, Ber. 6, 964); sp.gr. 2·151 at 0° (S.), 2·16439 at 0°, 2·13363 at 15·3°/0° (T.). From $CH_2I{\cdot}CH_2I$ and ICl; from C_2H_4 and an aqueous solution of ICl (Simpson, Proc. Roy. Soc. 12, 278). Decomposed by alcoholic KOH into HI and C_2H_3Cl; nascent H yields HCl, HI, and C_2H_4; moist Ag_2O at 160° produces glycol (Simpson). Finely divided silver at 160° yields C_2H_4 and $CH_2Cl{\cdot}CH_2Cl$ (Friedel and Silva, Bull. Soc chim. [ii.] 17, 242). Heated with HI solution, yields C_2H_4 and $C_2H_4I_2$ (Sorokin).

Ethylene cyanhydrin $HO{\cdot}CH_2{\cdot}CH_2CN$; b.p. 220°–222° at 723·5 mm.; sp.gr. 1·0588 at 0°. By long digestion of C_2H_4O (ethylene oxide) with anhydrous HCN at 50°–60° (Erlenmeyer, Annalen, 191, 273); miscible with alcohol and water; 100 parts ether dissolve 2·3 parts $C_2H_4(OH)CN$ at 15°; insoluble in CS_2. Forms a chloride with PCl_5, which boils at 174°–176° under 752 mm., and has sp.gr. 1·443 at

18·5° (Henry, Bull. Acad. Roy. Belg. iii. 35, 360).

Ethylene cyanide $C_2H_4(CN)_2$, *Succinonitrile*; m.p. 54·5° (Nevole and Tscherniak, Bull. Soc. chim. [ii.] 30, 101), 51°–52° (Henry, *ibid.* 43, 618); b.p. 158°–160° at 20 mm. (Pinner, Ber. 16, 360), 265°–267° (H.); sp.gr. 1·023 at 45°. By heating on a water-bath $CH_2Br{\cdot}CH_2Br$ with KCN and alcohol (sp.gr. 0·84) (Simpson, Proc. Roy. Soc. 10, 574); the liquid is filtered from the KBr, and distilled, when the alcohol is first removed; then the distillation is conducted under diminished pressure; also is produced by electrolysis of potassium cyanacetate (Moore, Ber. 4, 520); is a white amorphous mass soluble in water, chloroform, and alcohol; slightly in carbon disulphide and ether; decomposed when distilled at ordinary pressure. Decomposed by heating with KOH or HCl into NH_3 and succinic acid; with $AgNO_3$ forms plates of $C_2H_4(CN)_2,4AgNO_3$, which is soluble in water and alcohol, and explodes when heated (Simpson).

Ethylene diamine $NH_2{\cdot}C_2H_4{\cdot}NH_2$; m.p. 8·5° (Kraut, Annalen, 212, 251); b.p. 116·5°; sp.gr. 0·902 at 15° (Kraut). By heating $C_2H_4Cl_2$ or $C_2H_4Br_2$ with alcoholic NH_3 to 100° (Cloëz, J. 1853, 468); by distillation of *aβ*-diaminopropionic acid (Neuberg and Neimann, Zeitsch. physikal. Chem. 45, 110); by treatment of $C_2H_4(CN)_2$ with Sn and HCl (Fairley, Annalen, Suppl. 3, 372). 42 grams of $CH_2Cl{\cdot}CH_2Cl$ and 510 c.c. aqueous NH_3 are heated for 5 hours to 115°–120° in a sealed tube; the product is then evaporated until it begins to crystallise, and is then precipitated with 3 times its volume of absolute alcohol; the precipitated $C_2H_4(NH_2)_2,2HCl$ is then washed with alcohol and the base set free by distillation with powdered NaOH (Kraut, *l.c.*; also Hofmann, Ber. 4, 666). The by-product from the manufacture of chloral, consisting of $CH_2Cl{\cdot}CH_2Cl$, $CH_3{\cdot}CHCl_2$, &c., can be used. A thick oily liquid, with faint ammoniacal smell, soluble in water, not miscible with ether or benzene; the aqueous liquid, which contains $C_2H_4(NH_2)_2,H_2O$, cannot be freed from water by BaO, but only by distillation over Na. Caro's acid oxidises it to glyoxime (Bamberger and Seligman, Ber. 36, 3831). With HClO and HBrO, yields tetrachloro and tetrabromo derivatives; *e.g.* $Br_2N{\cdot}C_2H_4{\cdot}NBr_2$ (Chattaway, Chem. Soc. Trans. 1905, 381). Decomposed by HNO_2 into ethylene oxide and oxalic acid (Hofmann, J. 1859, 386); is a strong base and forms salts; combines with CS_2 to form crystals of

$$C_2H_4(NH_2)_2{\cdot}CS_2,$$

soluble in water, insoluble in alcohol and ether. $C_2H_4(NH_2)_2,2HCl$, long silvery needles insoluble in alcohol. $C_2H_4(NH_2)2HCl,PtCl_4$, yellow leaflets, slightly soluble in water (Greiss and Martius, Annalen, 120, 327); $C_2H_4(NH_2)_2(HCNS)_2$, large prisms, very soluble in water, m.p. 145° (Hofmann, Ber. 5, 245). Forms many compounds with metallic salts and a periodide $C_2H_4(NH_2)HI{\cdot}I_4$, which melts at 218°.

Diethylene diamine, *Piperazine*

$$(C_2H_4)_2(NH)_2 \text{ or } C_2H_4\begin{<}{NH \atop NH}\end{>}C_2H_4;$$

m.p. 104° (Berthelot); b.p. 170° (Hofmann, J. 1858, 343), 145°–146° (Berthelot), 140° (Rosdalsky). From ethylene chloride and alcoholic NH_3 (Cloëz; Hofmann, Natanson, Annalen, 98, 291); from sodium ethylene glycollate and acid derivatives of ethylene diamine by heating at 250°–850° (D. R. P. 67811); by heating the sodium compound of *sym*-diacyl ethylene diamine with anhydrous glycol or ethylene bromide at 200° (D. R. P. 73354); by reduction of ethylene oxamide with zinc-dust and KOH (D. R. P. 66461). (For other methods of preparation, *see* D. R. P. 70055, 70056, 73125, 74628, 79121, 98031, 100232.)

Forms a hydrate $C_4H_{10}N_2,6H_2O$; m.p. 44° (Berthelot). Piperazine is not changed by heating with HCl or H_2SO_4 at 200°. With carbonyl chloride it forms tricarbonyl piperazine. It forms a periodide $C_4H_{10}N_2{\cdot}2HI{\cdot}I_4,3H_2O$, m.p. 283°. The anhydrous periodide melts at 280° (Herz, Ber. 30, 1585). Piperazine reacts with 2 molecules HBrO to form an additive compound, which, on treatment with dilute alkali or piperazine solution, yields *n*-dibromopiperazine. This latter can form an additive compound with 2 molecules of HBrO (Chattaway, Chem. Soc. Trans. 1905, 951). Piperazine reacts with an excess of EtI at temperature of water-bath to form triethyl piperazonium iodide; m.p. 240°. Colourless needles, insoluble in cold water, ligroin, C_2Cl_2, C_6H_6, and CS_2; soluble in warm alcohol (Van Rijn, Chem. Zentr. 1898, 1, 727) (*v. Piperazine*).

***sym*-Diethylene diethyldiamine**

$$(C_2H_4)_2(NH{\cdot}C_2H_5)_2,H_2O;$$

b.p. 165° (Schmidt and Wichmann, Ber. 24, 3247); from $(C_2H_4)_2(NH_2)_2$ and C_2H_5I, or from $C_2H_4Br_2$ and $NH_2{\cdot}C_2H_5$ (Hofmann, J. 1859, 389); from piperazine and an excess of $KEtSO_4$ in aqueous solution (Van Rijn, Chem. Zentr. 1898, i. 727). It combines with salts of Cd, Cr, Zn, and Ni.

***as*-Diethylene diethyldiamine**

$$NH_2{\cdot}C_2H_4{\cdot}N(C_2H_5)_2;$$

mobile liquid; b.p. 145°; sp. gr. 0·827 at 18·5°/18·5°; from bromethylphthalimide and diethylamine with subsequent hydrolysis, yields a *platinochloride*, m.p. 230°; an *aurochloride*, m.p. 161°-163°; and a *picrate*, m.p. 211° (Ristenpart, Ber. 1896, 29, 2526).

Triethylene diamine $(C_2H_4)_3N_2$; b.p. 210°; soluble in water (Hofmann, J. 1858, 343, Harries, Annalen, 294, 350).

Diethylene triamine

$$NH_2{\cdot}C_2H_4{\cdot}NH{\cdot}C_2H_4{\cdot}NH_2;$$

b.p. (with slight decomposition) 208°; formed with other products by action of NH_3 upon $C_2H_4Br_2$; the double salt with $PtCl_4$ being less soluble than that of triethylene triamine, it can be separated from that body (Hofmann, J. 1861, 514).

A strongly alkaline liquid miscible with water and alcohol. Its salts are soluble in water, less so in alcohol, $2[(C_2H_4)_2N_2H_3,3HCl]3PtCl_4$ forms golden-yellow needles.

Triethylene triamine

$$C_2H_4\begin{<}{NH{\cdot}C_2H_4 \atop NH{\cdot}C_2H_4}\end{>}NH;$$

b.p. 216° (Hofmann, J. 1861, 514); forms salts; $[(C_2H_4)_2H_2N_2,3HCl]_2PtCl_4$; long golden-yellow needles moderately soluble in water; with

hydrobromic acid gives $(C_2H_4)_3N_2H_3,3HBr$ from acid solutions; from weaker acid solution $(C_2H_4)_3N_2H_3,2HBr$.

Tetraethylene triamine $(C_2H_4)_4N_3H_3$; by action of alcoholic NH_3 upon $C_2H_4Br_2$ (Hofmann, Ber. 3, 762); forms 3 series of salts with 1, 2, or 3 molecules of monobasic acid; the hydrobromides are amorphous bodies, almost insoluble in water, alcohol, and ether.

Triethylene tetramine

$$NH_2{\cdot}C_2H_4{\cdot}NH{\cdot}C_2H_4{\cdot}NH{\cdot}C_2H_4{\cdot}NH_2;$$

m.p. +12°; b.p. 266°–267°; sp.gr. 0·9817 at 15°; a strongly alkaline syrup from $C_2H_4Cl_2$ and $C_2H_4(NH_2)_2$, or from $C_2H_4Br_2$ and alcoholic NH_3 (Hofmann, J. 1861, 519); yields

$$C_6H_{18}N_4{\cdot}4HCl{\cdot}2PtCl_4;$$

a yellow amorphous powder almost insoluble in water.

Ethylene diformin $C_2H_4(CHO_2)_2$; b.p. 174°; by heating glycol with pure formic acid (Heninger, Ber. 7, 263); also by heating oxalic acid with glycol (Lorin, Bull. Soc. chim. [ii.] 22, 104). Decomposed when heated at 220° in sealed tube into CO_2, CO, H_2O, and C_2H_4.

Ethylene ferrous chloride $C_2H_4FeCl_2,2H_2O$; by heating $FeCl_2$ and ether to 150° (Kachler, Ber. 2, 510); forms prisms fairly soluble in water. The corresponding compound

$$C_2H_4FeBr_2,2H_2O$$

is prepared by leading C_2H_4 into a strong aqueous solution of $FeBr_2$ in sunlight (Chojnacki, Zeitsch. Chem. 1870, 420); forms light-green deliquescent crystals.

Ethylene iodide $CH_2I{\cdot}CH_2I$; m.p. 81°–82° (Aronstein and Kramps, Ber. 13, 489); sp.gr. 2·07; from C_2H_4 and I in sunlight (Faraday, Gm. 4, 682), also in the shade, especially if warmed (Regnault, Annalen, 15, 67); a mixture of I and alcohol (absolute) is saturated with C_2H_4 with repeated agitation (Semenow, J. 1864, 483).

Crystalline plates or prisms decomposed by heating; when warmed with alcohol to 70°, $IC_2H_4{\cdot}OC_2H_5$ is produced; $HgCl_2$ gives in the cold C_2H_4ICl, and on heating $C_2H_4Cl_2$ (Maumené, J. 1869, 345); alcoholic KOH converts it into C_2H_3I (Regnault, Annalen, 15, 63).

Ethylene iodohydrin $CH_2I{\cdot}CH_2OH$; from $C_2H_4(OH)_2$ and gaseous HI (Simpson, *ibid.* 113, 121); also by heating $C_2H_4(OH)Cl$ with KI (Butlerow and Ossokin, *ibid.* 144, 42).

An oil, b.p. 85°/25 mm.; sp.gr. 2·1649 at 18·6° (Henry, Ber. 24 Ref. 75).

Ethylene nitrate $NO_3CH_2{\cdot}CH_2{\cdot}NO_3$; b.p. 114°–116° with explosion (Demjanow, Chem. Zentr. 1899, i. 1064); sp.gr. 1·5099 at 4°, 1·4960 at 15°, 1·4860 at 25° (Perkin). Is formed when glycol is treated with HNO_3 and H_2SO_4, also by interaction of C_2H_4 and N_2O_5 in the cold (Demjanow); an oily liquid which is inflammable, explodes on percussion, and is poisonous; KOH converts it into alcohol (Henry, Ber. 3, 529; also Champion, Compt. rend. 73, 571). On reduction yields CH_2CHO, $C_2H_4(NH_2)_2$, and $H_2N{\cdot}CH_2{\cdot}CH_2OH$.

Ethylene nitrite

$$C_2H_4(NO)_2 \text{ or } NO_2{\cdot}CH_2CH_2{\cdot}NO_2;$$

m.p. below −15°; b.p. 96·8°; sp.gr. 1·2156 at 0° Bertoni). Is prepared by distilling glycerol trinitrite with more than an equivalent amount of glycol. Soluble in alcohol to form C_2H_5ONO (Bertoni, Gazz. chim. ital. 15, 353); insoluble in and slowly decomposed by water.

Ethylene oxide $\begin{matrix}CH_2\\ |\\ CH_2\end{matrix}\!\!>\!O$; b.p. 12·5°; sp.gr. 0·8909 at 4°/4°; 0·8824 at 10°/10° (Perkin, Chem. Soc. Trans. 1893, 488). From $C_2H_4(OH)Cl$ and KOH (Wurtz, Annalen, 110, 125; Ann. Chim. Phys. [3] 69, 317); also from $C_2H_4(OH)Cl$ and $C_2H_4(OH)ONa$ (Scheitz, Zeitsch. Chem. 1868, 379); also from $C_2H_4I_2$ and Ag_2O at 150°; from $C_2H_4Br_2$ and Ag_2O at 250°; or from $C_2H_4Br_2$ and Na_2O at 180° (Greene, J. 1877, 522); also by treatment of $C_2H_4Cl(OC_2H_3O)$ with KOH (Demole, Annalen, 173, 125); by dropping chlorethylacetate on to a cooled mixture of powdered KOH and sand (Roithner, Monatsh. 15, 666).

A pleasant-smelling liquid miscible with water; when heated with water in a closed tube, yields glycol, and polyethylene glycol. Has strong basic properties, although not an alkaline reaction. It combines with acids, and precipitates metallic hydroxides from solutions of Mg, Al, Fe, and Cu salts. With Na amalgam forms C_2H_6O. Pt black oxidises it to glycollic acid; PCl_5 produces $CH_2Cl{\cdot}CH_2Cl$ (Wurtz, Ann. Chim. Phys. [3] 69, 317, and 355).

Equal molecules of C_2H_4O and Br at 0° form $C_2H_4(OH)Br$, $C_2H_4Br_2$ and other bodies (Demole, Ber. 9, 47), but 2 molecules C_2H_4O and 1 molecule Br, on standing, yield large red or small yellow prisms of $(C_2H_4O)_2Br_2$; m.p. 65°; b.p. with decomposition at 95°; they are insoluble in water, but soluble in alcohol. H_2S or contact with Hg separates the Br and leaves dioxyethylene (Wurtz, Ann. Chim. Phys. [3] 69, 321). By long contact with $ZnCl_2$ or KHO, a polymeride which melts at 56° and is insoluble in ether, is produced (Wurtz, Bull. Soc. chim. [ii.] 29, 530).

Dioxyethylene, *Diethylene dioxide* $\begin{matrix}CH_2{\cdot}O{\cdot}CH_2\\ |\quad\quad |\\ CH_2{\cdot}O{\cdot}CH_2\end{matrix}$; m.p. 9°; b.p. 102°; sp.gr. 1·0482 at 0°. From $(C_2H_4)_2O_2{\cdot}Br_2$, and Hg by contact at ordinary temperature. The mixture is then distilled, and distillate rectified over KOH (Wurtz, Ann. Chim. Phys. [3] 69, 323); has no marked basic properties, but combines slightly with acetic acid on heating to 120°. Lourenço (*ibid.* [3] 67, 288) obtained it by heating $C_2H_4(OH)_2$ and $C_2H_4Br_2$ to 160°, but the product boiled at 95°. Forms an iodide with 2 atoms of I, m.p. 84°, which is decomposed by water and air, but soluble in benzene; also a sulphate and a picrate melting respectively at 100° and 66°. It also forms a compound with $HgCl_2$, soluble in, but slowly decomposed by, water (Faworsky, J. Russ. Phys. Chem. Soc. 38, 741; Paternò and Spallino, Atti. R. Acad. Lincei, [v.] 16, i. 87).

Chlorethylene oxide C_2H_3ClO; b.p. 70°–80°. By long contact of acetylene chloriodide CHCl:CHI with 40–50 vols. of water at 200°–220° (Sabanejeff, Annalen, 216, 268); difficultly soluble in water.

Bromethylene oxide $C_2H_3Br{\cdot}O$; b.p. 89°–92°. From bromoglycol bromhydrin $CHBr_2{\cdot}CH_2OH$ and KOH (Demole, Ber. 9, 51); soluble in water.

Ethylene phosphides *v.* PHOSPHORUS, ORGANIC COMPOUNDS OF.

Ethylene selenocyanate $C_2H_4(SeCN)_2$; m.p. 128° (Proskauer), 138° (Hagelberg, Ber. 23, 1092). From $CH_2Br{\cdot}CH_2Br$ and alcoholic KCNSe (Proskauer, *ibid.* 7, 1281). Colourless needles, insoluble in cold water or ether, difficultly soluble in hot water or cold alcohol; dissolves unchanged in strong HNO_3, but on heating gives ethylene selenious acid $C_2H_4(SeO_3H)_2$. With alcoholic alkali, yields ethylene diselenide (Hagelberg).

Diethylene disulphide $S<\begin{matrix}CH_2{\cdot}CH_2\\CH_2{\cdot}CH_2\end{matrix}>S$; m.p. 111°–112°; b.p. 199°–200°; V.D. =4·28 (Husemann, Annalen, 126, 280). From $C_2H_4Br_2$ and K_2S (Crafts, *ibid.* 124, 110; 128, 220); also by heating $C_2H_4CS_3$ or $C_2H_4S_2Hg$ with $C_2H_4Br_2$ at 150° (H.).

Crystallises from alcohol in needles or leaflets, from ether in thick prisms which are volatile at ordinary temperatures; combines with Br and certain salts, but not with NH_3; oxidised by HNO_3 to $(C_2H_4)_2S_2O_2$. The bromide

$$(C_2H_4)_2S_2Br_4$$

is a lemon-yellow amorphous body, m.p. 96°, very unstable; the iodide $(C_2H_4)_2S_2I_4$, m.p. 132°–133°, forms iron-black monoclinic needles, insoluble in water. The oxide $(C_2H_4)_2S_2O_2$ can also be obtained by decomposition of the chloride or bromide; with water, forms crystals which decompose without fusion on heating, and are soluble in water, almost insoluble in alcohol. The peroxide $(C_2H_4)_2S_2O_4$, obtained by heating $(C_2H_4)_2S_2$ with fuming HNO_3 to 150° (Crafts, Annalen, 125, 124), crystallises from strong HNO_3 in small crystals which are insoluble in water.

Ethylene hydroxysulphide $C_2H_4(OH)SH$ (*Thioethylene glycol*), from $HO{\cdot}CH_2CH_2Cl$ and alcoholic KHS; the KCl is filtered off and the filtrate acidified with dilute HCl and evaporated at 30°–40° (Carius, Annalen, 124, 258). Is a heavy liquid, almost insoluble in water, soluble in alcohol; the salts are fairly soluble in alcohol; the mercury compound $Hg(C_2H_5OS)_2$ crystallises from alcohol in needles.

Thiodiethylene glycol $(C_2H_4OH)_2S$ is formed when the above compound is heated, H_2S being evolved. It is a crystalline solid; m.p. under 60°, soluble in alcohol, insoluble in water, forms salts and double compounds with metallic salts.

Ethylene mercaptan $C_2H_4(HS)_2$; b.p. 146°; sp.gr. 1·123 at 23·5°. From $CH_2Cl{\cdot}CH_2Cl$ (or bromide, Werner, J. 1862, 424) and alcoholic KHS (Löwig and Weidmann, Annalen, 36, 322). A colourless liquid, soluble in alcohol and alkalis, forms insoluble mercaptides with heavy metals. $Pb(C_2H_4)S_2$ yellow; $Cu(C_2H_4)S_2$ chrome green. *Ethylene dimethyl sulphide* $C_2H_4(SCH_3)_2$, b.p. 183°, from $C_2H_4Br_2$ and CH_3SNa (Ewerlöf, Ber. 4, 716). *Ethylene diethyl sulphide* $C_2H_4(SC_2H_5)_2$, b.p. 210°–213° (E.) gives on oxidation first $(C_2H_5SO)_2C_2H_4$, m.p. 170°; and next $(C_2H_5SO_2)_2C_2H_4$, m.p. 136·5° (Beckmann, J. pr. Chem. [2] 17, 469).

Ethylene thiocarbonates.

1. *Ethylene dithiocarbonate* $C_2H_4COS_2$, *ethylene oxythiocarbonate*; m.p. 31°; by action of HNO_3 upon $C_2H_4CS_3$ in the cold (Husemann, Annalen, 126, 269); forms long thin tables, insoluble in water, soluble in alcohol, ether, and chloroform.

2. *Ethylene trithiocarbonate* $C_2H_4CS_3$; m.p. 39·5° (Husemann), 33·4° (Konowalow), 39° (Frasetti); sp.gr. 1·4768. From $C_2H_4Br_2$ and Na_2CS_3 in presence of absolute alcohol (Husemann, Annalen, 123, 83); by action of water upon $AlBr_3{\cdot}C_2H_4Br_2{\cdot}CS_2$ (Konowalow); by action of alcoholic KOH upon ethylene xanthate

$$C_2H_4(S{\cdot}CS{\cdot}OEt)_2+KOH = KS{\cdot}CO{\cdot}OEt+C_2H_4CS_3+EtOH,$$

a theoretical yield; it reacts with dil. KOH thus:

$$C_2H_4CS_3+EtOH+3KOH = KS{\cdot}CO{\cdot}OEt+C_2H_4S_2K_2+2H_2O$$

(Frasetti, Ber. 38, 488). Forms golden-yellow, rhombic prisms; slowly soluble in alcohol, easily soluble in ether, very soluble in CS_2, $CHCl_3$, and C_6H_6.

Ethylene thiochlorides (Guthrie, Chem. Soc. Trans. 1861, 13, 35; 1862, 14, 128).

1. *Ethylene thiodichloride* $C_2H_4SCl_2$, by passing C_2H_4 into cooled SCl_2. Is a liquid with a smell resembling mustard oil, and is decomposed on heating.

2. *Ethylene dithiodichloride* $(C_2H_4)_2S_2Cl_2$, by action of C_2H_4 upon S_2Cl_2 at 100°. A liquid with a pungent odour.

Chlorethylene dithiodichloride $(C_2H_3Cl)_2S_2Cl_2$; by action of C_2H_4 upon boiling S_2Cl_2; a light-yellow liquid with pleasant smell.

Ethylenethiocyanate $C_2H_4(SCN)_2$; m.p. 90°. From $CH_2Cl{\cdot}CH_2Cl$ and alcoholic KCNS (Sonnenschein, J. 1855, 609; Buff, Annalen, 100, 229); $CH_2Br{\cdot}CH_2Br$ may be used with advantage (Glutz, *ibid.* 153, 313); forms rhombic plates slightly soluble in cold water, more so in hot, and in alcohol, decomposed by heat, volatile in steam; its vapour excites tears.

Ethylidene acetamide $CH_3CH(NHC_2H_3O)_2$; m.p. 169°; formed by acting on acetamide with aldehyde; forms large prisms decomposed by acids (Tawildarow, Ber. 5, 477).

Ethylidene acetate $CH_3{\cdot}CH(C_2H_3O_2)_2$; b.p. 169°; sp.gr. 1·061 at 12°. From aldehyde and $(C_2H_3O)_2O$ at 180° (Geuther, Annalen, 106, 249); from alcoholic $C_2H_3O_2K$ and $CH_3CHCl{\cdot}C_2H_3O_2$ (Schiff, Ber. 9, 304); has a smell like that of onions, and is decomposed by water into aldehyde and acetic acid.

Ethylidene azine $CH_3CH{:}N{\cdot}N{:}CHCH_3$; b.p. 95°–96° at 760 mm.; sp.gr. 0·832 at 17°. Prepared by shaking an ethereal solution of aldehyde with an aqueous solution of hydrazine hydrate. At 180° it is unchanged, but at a higher temperature gives off nearly all its N as gas. It is fairly stable to alkalis, but is hydrolysed by acids into aldehyde and hydrazine (Curtius and Linkeisen, J. pr. Chem. 1898, [ii.] 58, 310).

Ethylidene biuret $NH<\begin{matrix}CO{\cdot}NH\\CO{\cdot}NH\end{matrix}>CH{\cdot}CH_3$, *Trigenic acid*, by leading HCNO into well-cooled aldehyde (Liebig and Wöhler, Annalen, 59, 296), crystallises in small prisms, slightly soluble in water, nearly insoluble in alcohol, has a slightly acid taste. When heated, liberates CO_2, NH_3, and traces of collidine $C_8H_{11}N$ (Herzig, Monatsh. 2, 398). Is hardly decomposed by NaBrO. HNO_3 decomposes it and liberates cyanuric acid. The silver compound $AgC_4H_6N_3O_3$ forms amorphous precipitate, soluble in boiling water.

Ethylidene bromide $CH_3{\cdot}CHBr_2$, b.p. 114°–115° (Tawildarow, *ibid.* 176, 12), 109°–110° at 751 mm. (Denzel, *ibid.* 195, 202), 110·5° at

760 mm. (Anschütz, *ibid.* 221, 137), 108°–110° (corr.) (Perkin, Chem. Soc. Trans. 45, 523); b.p. 107°–108° (V. Meyer and Muller, J. pr. Chem. [2] 46, 168); sp.gr. 2·129 at 10° (T.), 2·1001 at 17·5°/4°, 2·0891 at 20·5°/4° (Anschütz) 2·0822 at 21·5°/4°, 2·1029 at 15°, 2·0854 at 25° (P.). From C_2H_5Br and Br at 170° (Hofmann, Proc. Roy. Soc. 10, 619; Caventou, Compt. rend. 52, 1330). Is produced by action of PCl_3Br_2 but not of PBr_5 upon aldehyde (Paternò and Pisati, Ber. 5, 289); also by heating CH_2:CHBr with HBr to 100° (Reboul, Compt. rend. 70, 398). A heavy liquid; alcoholic KHS has no action upon it. On heating with water and PbO to 130°, aldehyde and HBr are produced (T.). With $SbCl_5$ gives CH_3·$CHCl_2$ (Henry, Bull. Soc. chim. [ii.] 42, 262).

Ethylidene bromiodide CH_3CHBrI; m.p. below −20°; b.p. 142°–143°; sp.gr. 2·50 at 1°, 2·452 at 16°. From C_2H_3Br and HI in the cold (Pfaundler, J. 1865, 483; Reboul, Annalen, 155, 212); by shaking CH_3CHI_2 with IBr solution (Simpson, Bull. Soc. chim. [ii.] 31, 412); decomposed by alcoholic KOH or Ag_2O into HI and C_2H_3Br; Br yields CH_3CHBr_2.

Ethylidene chlorobromide $CH_3CHClBr$; m.p. 16·6° (corr.) (Schneider, Zeitsch. physikal. Chem. 19, 157); b.p. 84°–84·5° at 750 mm., 82·7° at 760 mm. (Städel, Ber. 15, 2563); sp.gr. 1·667 at 16°. From C_2H_3Br and concentrated HCl at 100° (Reboul, Annalen, 155, 215); from C_2H_5Cl and Br in sunlight (Denzel, *ibid.* 195, 193). By action of Cl upon C_2H_5Br (Lescœur, Bull. Soc. chim. [ii.] 29, 483). Is decomposed at ordinary temperature by alcoholic KOH on long standing; with Ag_2O gives aldehyde; and with $AgC_2H_3O_2$ forms $CH_3CH(C_2H_3O_2)_2$ (L.).

Ethylidene chloriodide CH_3CHClI; b.p. 117°–119°; sp.gr. 2·054 at 19°. By agitating a mixture of CH_3CHI_2 and ICl; formed also from CH_3CHCl_2 and Al_2I_6 (Simpson, Bull. Soc. chim. [ii.] 31, 411).

Ethylidene or Ethidene chloride CH_3CHCl_2; m.p. −101·5° (Schneider, Zeitsch. physikal. Chem. 22, 233), b.p. 59·9° (corr.), sp.gr. 1·2044 at 0°, 1·1863 at 12·24°/4° (Thorpe, Chem. Soc. Trans. 37, 183); b.p. 57·4°–57·6° at 750·9 mm., sp.gr. 1·1743 at 20°/4° (Brühl, Annalen, 203, 11), 1·2124 at 0°, 1·1805 at 22°/0°; refractive index μ_A (at 24·7°) = 1·405724. R_α = 34·1 (Kanonnikow); b.p. 57°–57·7° at 738·7 mm., sp.gr. 1·2013 at 0° (Pribram and Handl, Monatsh. 2, 650); b.p. 56·7°–56·9° at 749·1 mm., sp.gr. 1·1895 at 9·8°/4°, 1·11425 at 56·7°/4° (R. Schiff, Annalen, 220, 96); crit. temp. 254·5° (Pawlewsky, Ber. 16, 2633); H.C.p. = 267·1 cals. (Berthelot and Ogier, Bull. Soc. chim. [ii.] 36 68). From C_2H_5Cl and Cl (Regnault, Annalen, 33, 312); from C_2H_4O and PCl_5 (Beilstein). By action of HCl upon copper acetylene (Sabanejeff, *ibid.* 178, 111). Is prepared by passing a mixture of chlorine and C_2H_5Cl over animal charcoal heated to 250°–400° (Damoiseau, Bull. Soc. chim. [ii.] 27, 113). Is obtained as a by-product in the manufacture of chloral. Is decomposed by alcoholic KOH into HCl and C_2H_3Cl. Sodium produces at 180°–200° hydrogen, acetylene, ethylene, ethane, and C_2H_3Cl (Tollens, Annalen, 137, 311). By action of Cl, CH_2CCl_2 and CH_2Cl·$CHCl_2$ are produced.

Ethylidene di-*iso*-nitramine is formed by the interaction of $CO(Et)_2$, or COEtMe, and NO, in C_2H_5ONa. The lead salt is anhydrous and crystallises in cubes. The dimethyl ether forms rhombic crystals, and melts at 75°. The *iso*-nitramine itself is hydrolysed by mineral acids into acetaldelyde NH_2OH and oxides of N. With Na amalgam, is reduced to hydrazine (Traube, Annalen, 300, 120).

Ethylidene diethyl ether

CH_3·$CH(OC_2H_5)_2$ (*v.* ACETAL).

Ethylidene dimethyl ether $CH_3CH(OCH_3)_2$, *Dimethyl acetal*; b.p. 64·4° (Dancer, Annalen, 132, 240), 62·7°–63·3° at 757·6 mm. (R. Schiff, *ibid.* 220, 104); sp.gr. 0·8787 at 0°, 0·8590 at 14°, 0·8476 at 25° (D.), 0·8013 at 62·7°/4° (S.); capillarity constant at b.p. a^2 = 4·092 (Schiff, Annalen, 223, 74); occurs in crude wood spirit (D.): 2 volumes of wood spirit, 1 volume aldehyde, and ¼ volume of glacial acetic acid are heated to 100° (Alsberg, J. 1864, 485); also by oxidation of CH_3OH and C_2H_5OH by MnO_2 and H_2SO_4 (Wurtz).

Ethylidene methyl propyl ether

CH_3·$CH(OCH_3)(OC_3H_7)$;

b.p. 103°–105° (Bachmann, Annalen, 218, 46).

Ethylidene ethyl propyl ether

CH_3·$CH(OC_2H_5)(OC_3H_7)$;

b.p. 124°–126° (Bachmann, *l.c.*).

Ethylidene dipropyl ether CH_3·$CH(OC_3H_7)_2$; b.p. 146°–148°, sp.gr. 0·825 at 22° (Girard, J. 1880, 695).

Ethylidene methyl *iso*butyl ether

CH_3·$CH(OCH_3)(OC_4H_9)$;

b.p. 125°–127° (Claus and Trainer, Ber. 19, 3005; Bachmann, *l.c.*).

Ethylidene ethyl *iso*butyl ether

CH_3·$CH(OC_2H_5)(OC_4H_9)$;

b.p. 155° (Claus and Trainer, *l.c.*).

Ethylidene *di iso*butyl ether CH_3·$CH(OC_4H_9)_2$; b.p. 168°–170, sp.gr. 0·816 at 22° (Claus and Trainer, *l.c.*; Girard, *l.c.*).

Ethylidene methyl *iso*amyl ether

CH_3·$CH(OCH_3)(OC_5H_{11})$;

b.p. 141°–144° (Bachmann, *l.c.*).

Ethylidene ethyl *iso*amyl ether

CH_3·$CH(OC_2H_5)(OC_5H_{11})$;

b.p. 165°–167° (Claus and Trainer, *l.c.*).

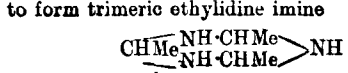
Ethylidene *di iso*amyl ether

$CH_3CH(OC_5H_{11})_2$;

b.p. 210·8° (corr.), sp.gr. 0·8347 at 15° (Claus and Trainer, *l.c.*).

Ethylidene hydramine CH_3·$CH(OH)NH_2$ *v. Aldehyde-ammonia*, art. ALDEHYDE.

Ethylidene imine $CH_3CH{:}NH$; m.p. about 85°; b.p. 123°–124°. If aldehyde ammonia be kept *in vacuô* over H_2SO_4 for several days, the imine is formed. It crystallises in brilliant colourless crystals, which have an odour like acetamide. It is soluble in water, EtOH, CH_3COOH, $CHCl_3$, C_6H_6, and toluene. The vapour density at 260° agrees with the simple formula, but at lower temperatures the V.D. is higher. It forms a picrate, and combines with HCN to form CH_3·$CH(NH_2)CN$. It polymerises to form trimeric ethylidine imine



which forms a trinitroso- derivative, with N_2O_3 in $CHCl_3$; opaque yellow-white needles,

melting at 161° (Delépine, Compt. rend. 1897, 125, 951; and 1907, 144, 853).

Ethylidene iodide CH_3CHI_2; b.p. 177°–179°; sp.gr. 2·84 at 0°. By combination of C_2H_2 and HI (Berthelot, Annalen, 132, 122; Semenow, Zeitsch. Chem. 1865, 725); from CH_3CHCl_2 and Al_2I_6 (Gustavson, J. Russ. Phys. Chem. Soc. 6, 164); from C_2H_3Br and HI (Friedel, Ber. 7, 823). Decomposed by alcoholic KOH into HI and C_2H_3I.

Ethylidene malonic acid $CH_3{\cdot}CH{:}C(COOH)_2$; only known in combination, the *ethyl ester* $CH_3CH:C(COOC_2H_5)_2$, b.p. 220°, 115°–118° at 17 mm.; sp.gr. 1·0435 at 15°. From $CH_2(CO_2Et)_2$ (1 mol.) aldehyde (2 mols.), and $(C_2H_3O)_2O$ (1½ mols.) at 100° (Komnenos, Annalen, 218, 157). An ethereal oil smelling of camphor; by long contact with $Ba(OH)_2$ in the cold yields ethoxy malonic acid $C_5H_8O_5$, malonic acid $C_3H_4O_4$, and aldehyde.

Ethylidene oxide $CH_3{\cdot}CHO$ *v.* ALDEHYDE.

Ethylidene ethylene oxide

$$CH_3{\cdot}CH\begin{matrix}OCH_2\\ \\ OCH_2\end{matrix}$$

b.p. 82° (Verley, Bull. Soc. chim. [iii.] 21, 276), 82·5° at 765·8 mm.; sp.gr. 1·002 at 0°. From aldehyde and excess of glycol at 100° (Wurtz, Compt. rend. 53, 378; Annalen, 120, 328); a liquid with irritating smell, soluble in 1½ vols. water, from which $CaCl_2$ separates it; with acetic acid gives glycol diacetate.

Ethylidene ethoxyacetate $CH_3CH(OEt)OAc$; b.p. 125°–130°; sp.gr. 0·941. By heating together acetal and acetic anhydride for 3 hours at 150°. A pleasant-smelling oil, slowly decomposed by cold water into alcohol, aldehyde, and acetic acid, rapidly on boiling.

Ethylidene sulphonic acids.

1. *Ethylidene hydroxysulphonic acid*

$$CH_3CH(OH)(HSO_3).$$

Salts of this acid are formed by action of aldehyde upon alkaline hydrogen sulphites; they are crystalline bodies, soluble in water, and decomposed on heating into water, aldehyde, and sulphites.

2. *Ethylidene chlorsulphonic acid*

$$CH_3{\cdot}CH{\cdot}Cl(SO_3H)$$

obtained by action of CH_3CHCl_2 upon neutral alkaline sulphites at 140°; the salts are crystalline, and the acid is fairly stable.

3. *Ethylidene disulphonic acid*

$$CH_3CH(SO_3H)_2.$$

By oxidation of trithioaldehyde $(C_2H_4S_3)$ or thialdin by $KMnO_4$ solution (Guareschi, Gazz. chim. ital. 9, 75; Annalen, 222, 302). 10 grams thialdin are treated with 30–35 grams $ZnMn_2O_8$ and 300 grams water; after filtering, BaH_2O_2 is added and excess of Ba precipitated by CO_2; the Ba salt is then precipitated by alcohol. It forms a strongly acid oily liquid, very soluble in water and alcohol, and is very stable; forms stable salts $Na_2C_2H_4S_2O_6,H_2O$, small silky crystals soluble in 6071 parts of alcohol (90 p.c.) at 24·5°; $K_2C_2H_4S_2O_6,2H_2O$ forms large transparent crystals soluble in 1·56 parts of water at 17°.

ETHYL ACETATE *v. Alkyl acetates*, art. ACETIC ACID.

ETHYLBUTYLACETIC ACID *v.* OCTOIC ACIDS.

ETHYL-*iso*-BUTYLACETIC ACID *v.* OCTOIC ACIDS.

ETHYL BUTYRATE *v.* BUTYRIC ACID.

ETHYL DIPHENYLAMINE *v.* DIPHENYLAMINE.

ETHYLKETENE *v.* KETENES.

ETHYLKETENECARBOXYLATE *v.* KETENES.

ETHYLMALONIC ACID *v.* GLUTARIC ACID and MALONIC ACID.

ETHYLPROPYLACETIC ACID *v.* HEPTOIC ACIDS.

EUBORNYL. Trade name for bornyl-α-bromo-*iso*valerate, obtained by brominating chloro-*iso*valeric acid and esterifying borneol with the product. A syrupy aromatic liquid; b.p. 175°–178°. Used as a sedative (*v.* SYNTHETIC DRUGS).

EUCAINE, EUCHININ, EUCODIN, EUCOL, EUDOXIN *v.* SYNTHETIC DRUGS.

EUCAIRITE or **EUKAIRITE** *v.* SELENIUM.

EUCALYPTOL. The volatile oil of the leaves of *Eucalyptus globulus*, consists mainly of a body $C_{10}H_{18}O$; b.p. 176°–177°; sp.gr. 0·923 at 16°. It is optically inactive, has a camphor-like smell, and is probably identical with cineol and cajeputol (*v.* OILS, ESSENTIAL).

EUCALYPTUS OIL *v.* OILS, ESSENTIAL.

EUCLASE *v.* GLUCINUM.

EUGENOL $(HO)(CH_3O)C_6H_3{\cdot}CH_2{\cdot}CH:CH_2$ ($C_3H_5:CH_3O:HO=1:3:4$) occurs in oil of cloves from the leaves of *Eugenia caryophyllala* (Thunb.) (Bonastre and Ettling, Annalen, 9, 68); in the oil from the leaves of the Ceylon cinnamon tree (Stenhouse, Annalen, 95, 103; Schimmel & Co., Chem. Zentr. 1902, ii. 1486); from *Cinnamomum pedatinervium* (Meissn.) (Goulding, Chem. Soc. Trans. 1903, 1101), *C. Tamala* (Nees et Eberm.) (Schimmel & Co., Chem. Zentr. 1910, i. 1720), *C. cassia* (Plume), and *C. zeylanicum* (Nees) (Duyk, Chem. Zentr. 1896, ii. 358; Weber, Arch. Pharm. 230, 232); from the fruit of *Pimenta officinalis* (Lindl.) (Bonastre, *l.c.*; Oeser, Annalen, 131, 277); from the sap of *Acacia Farnesiana* (Willd.) (Walbaum, J. pr. Chem. 68, [2] 235); in the oil from *Ocimum Basilicum* (Linn.) (Schimmel & Co., Chem. Zentr. 1900, i. 906); in calamus oil (Thoms and Beckstroem, Ber. 1902, 3187); in Ylang Ylang oil (Schimmel & Co., Chem. Zentr. 1903, i. 1087; ii. 272); in olive oil from Pugli (Canzoneri, Gazz. chim. ital. 1897, 27, ii. 1); in oil of nutmeg (Power and Salway, Chem. Soc. Trans. 1907, 2041); in sassafras leaves and bark (Pomeranz, Monatsh. 11, 101; Power and Kleber, Chem. Zentr. 1897, ii. 42); in the oil from the leaves of the bay tree (Mittmann, Arch. Pharm. 27, [3] 539); in oil from Maltese oranges (Gildemeister and Stephan, Arch. Pharm. 235, 583), and in other ethereal oils. The methyl ether of eugenol

$$(CH_3O)_2C_6H_3{\cdot}CH_2{\cdot}CH:CH_2$$

occurs in the oil of *Asarum canadense* (Linn.) (Power and Lees, Chem. Soc. Trans. 1902, 67), of *A. arifolium* (Michx.) (Miller, Arch. Pharm. 240, 371); in oil from Paracoto bark (Jobst and Hesse, Annalen, 199, 75; Wallach and Rheindorff, *ibid.* 271, 300); in Ylang Ylang oil; in oil from the bark of *Cinnamomum pedatinervium*; in oil from Maltese oranges (*v. supra*); and in oil of citron (Schimmel & Co., Chem. Zentr. 1899, ii. 879).

Oil of cloves, which contains eugenol and a terpene as the chief constituents, is treated with potash; the potassium salt of eugenol separates, is pressed out, washed with alcohol, and the eugenol set free by the addition of a mineral acid (Wasserman, Annalen, 179, 369).

It is obtained by a similar process from oil of cinnamon leaves or from that of *Pimenta officinalis* (Lindl.). Another method consists in separating eugenol from oil of cloves by means of the compound it forms with sodium acetate (Chem. Werke Byk. D. R. P. 100418; Chem. Zentr. 1899, i. 764). In the former process, a residue is left after treating the oil of cloves with potash, and by distilling this under reduced pressure, acetyl eugenol, m.p. 29°, is obtained (Erdmann, J. pr. Chem. 1897, [2] 56, 146). By reducing coniferin in alkaline solution with sodium amalgam, eugenol is formed (Chiozza, Chem. Zentr. 1888, 443). Methyl eugenol (allyl guaiacol) has been prepared synthetically by treating veratrol (dimethylcatechol) with allyl iodide and zinc-dust (Moureau, Compt. rend. 121, 721).

Pure eugenol is a colourless oil; b.p. 244·5° (Frankforter and Lando, J. Amer. Chem. Soc. 27, 641), 247·5° (Wasserman, Annalen, 179, 366), 253·5° (corr.) (Perkin, Chem. Soc. Trans. 1896, 1247); sp.gr. 1·0785° at 4°/4°, 1·0734 at 10°/10°, 1·0663 at 20°/20°; specific magnetic rotation, 2·1974; molecular magnetic rotation at 15°, 18·727 (Perkin, *l.c.*); dielectric constant, 6·0 (Mathews, J. Phys. Chem. 9, 641); μ_D 1·54437; sp.heat, 0·5024; mol. heat of combustion, 1304 cals. (F. & L. *l.c.*). Eugenol reddens litmus, smells strongly of cloves, and has a burning taste. It does not reduce Fehling's solution, but reduces ammoniacal silver solutions on long standing. Eugenol may be detected by the following reactions: (i.) Ferric chloride imparts a blue colour to its alcoholic solution; (ii.) zinc chloride yields a transitory pale-yellow colour; (iii.) sulphuric acid gives first a brown colour, changing quickly to purple and finally to wine-red; (iv.) Burgess (Analyst, 1900, 25, 265) makes use of a reagent prepared by dissolving 10 grams of mercuric salt in 25 p.c. sulphuric acid, and making the solution up to 100 c.c. with the latter. By shaking 2 c.c. of eugenol with 5 c.c. of the reagent, and allowing the solution to stand, a pale violet colour is developed. (For estimation of eugenol in oil of cloves, *v.* Verley and Bölsing, Ber. 1901, 3359; Thoms. Chem. Zeit. 1903, 27, 954; Arch. Pharm. 241, 592; Spurge, Pharm. J. 1903, [4] 16, 701, 757; Schimmel & Co., Chem. Zentr. 1903, ii. 1124; Reich, Zeitsch. Nahr. Genussm. 1909, 18, 401.)

Eugenol and its derivatives are readily converted into the corresponding derivatives of the isomeric *iso*eugenol (*v. infra*), which on oxidation yields vanillin and its derivatives. Chromic acid oxidises eugenol to acetic acid, carbon dioxide, and water (Wassermann, *l.c.*); chromyl chloride, however, combines with eugenol, and on decomposing the product with water, vanillin can be extracted (Novarine, Amer. Pat. 365918, 365919; Ber. Ref. 1896, 812). Nitric acid oxidises eugenol to oxalic acid and a resin, but in ethereal solution, 5-nitro-eugenol is formed (*v. infra*). Ferric chloride oxidises it to dehydroeugenol, m.p. 105°–106° (Cousin and Hérissey, Compt. rend. 1908, 146, 1413). Oxidised with potassium permanganate, eugenol yields homovanillin, vanillin, and vanillic acid (Erlenmeyer, Ber. 1876, 273). Hydrogenisation of either eugenol or *iso*eugenol in the presence of platinum black, yields dihydroeugenol (propylguaiacol), b.p. 246°–248° (Fournier, Bull. Soc. chim. [4] 7, 23).

5-Nitroeugenol is prepared by acting on eugenol in ethereal solution with nitric acid. It forms large triclinic crystals, m.p. 43°–44° (Weselsky and Benedikt, Monatsh. 3, 388). With tin and hydrochloric acid, it produces aminochlorhydroeugenol hydrochloride; aminochlorhydroeugenol melts at 97°. Nitroeugenol, heated with acetic anhydride and sodium acetate, forms nitro-aceto-eugenol, m.p. 61°, which, oxidised by potassium permanganate at 70° (Tiemann, Ber. 1876, 418), yields *nitrovanillic acid* $C_6H_2(COOH)(OCH_3)(OH)NO_2$, decomposing at 210° without melting.

Acyl and *aryl derivatives* of eugenol are obtained by treating eugenol with acyl or aryl anhydrides in the cold, in presence of some condensing agent such as sulphuric acid, zinc chloride, pyridine, &c. The chlorides may be substituted for the anhydrides (Merck, D. R. PP. 103581, 109445; Chem. Zentr. 1899, ii. 927; 1900, ii. 407; Riedel, D. R. P. 189333; Chem. Zentr. 1908, i. 185; Pond & Beers, J. Amer. Chem. Soc. 19, 825). *Acetyl eugenol*, which occurs in oil of cloves (Erdmann, J. pr. Chem. 1897, [2] 56, 146), melts at 29°, and boils at 281°–282° (752 mm.) (Freyss, Chem. Zentr. 1899, i. 835); *benzyl eugenol* has b.p. 235°, and on heating with potash and subsequently with potassium dichromate and sulphuric acid, the benzyl ether of vanillin is obtained (Boehringer and Sons, D. R. P. 65937; Ber. Ref. 1893, 211). *Eugenol carbonate*, m.p. 93°–94°, is obtained by passing phosgene gas into an alkaline solution of eugenol; on treatment with ammonia, the carbamate is formed (F. von Heyden Nachf. D. R. P. 58129; Ber. Ref. 1892, 186); the carbonate can also be obtained from eugenol and the diphenyl ester of carbonic acid (D. R. P. 99057; Chem. Zentr. 1898, ii. 1190). On adding eugenol to a cooled mixture of pyridine and chlorsulphonic acid in carbon disulphide, *potassium eugenyl sulphate*, m.p. 203°, is obtained; the latter is transformed by heating with excess of potash into potassium *iso*eugenyl-sulphate, m.p. 223°, which, on oxidation with ozone, yields potassium vanillin sulphate (Verley, Bull. Soc. chim. 1901, [3] 25, 46).

Eugenyl acetic acid

$C_6H_3(CH_2{\cdot}CH{:}\ CH_2)(OCH_3)(OCH_2{\cdot}CO_2H)$

is obtained by heating eugenol with chloracetic acid in the presence of sodium hydroxide for 20 hours, and decomposing the sodium salt thus formed with hydrochloric acid; m.p. 75°. By heating the acid with potash and amyl alcohol at 150°, *iso*eugenyl acetic acid, m.p. 92°–94°, is produced; and oxidation of the latter with potassium permanganate yields vanillin acetic acid (Gassmann and Krafft, Ber. 1895, 1870).

Eugenyl phosphoric acid is obtained by treating eugenol with phosphorus oxychloride and decomposing the resulting chloride with water; m.p. of anhydrous acid, 105° (Boehringer & Sons, D. R. P. 98522; Chem. Zentr. 1898, ii. 950; Oeser, Annalen, 131, 277). On heating with alcoholic potash, *iso*eugenyl phosphoric acid is obtained, and by heating the acid sodium salt of the latter to 150°, *iso*eugenol is obtained quantitatively.

Eugenyl alcohol is prepared by heating eugenol in 20 p.c. sodium hydroxide solution with formaldehyde at 60°; m.p. 37°–38° (Morasse, Ber. 1902, 3894).

Eugenol glucoside, m p. 132°, is produced by the action of acetochlorhydrose on the potassium salt of eugenol (Michael, Amer. Chem. J. 6, 336).

Eugenol and *iso*eugenol form compounds with proteids which are stated to be used in the treatment of tuberculosis (Belart, Eng. Pat. 9246, 26075; Fr. Pat. 389889; J. Soc. Chem. Ind. 1908, 998; 1909, 1325).

(For compounds with iodine, *v.* F. v. Heyden Nachf. D. R. P. 70058; Ber. Ref. 1893, 915; Ingle, J. Soc. Chem. Ind. 1904, 422.) The *N*-substituted aminoethyl compounds of eugenol- and *iso*eugenol- acetamide are stated to be used as local anæsthetics (Einhorn, D. R. P. 208255; J. Soc. Chem. Ind. 1909, 491).

Bromine in excess forms with eugenol, dibromeugenol dibromide, m.p. 118°–119°, which, treated with zinc-dust in alcoholic solution, yields dibromeugenol, m.p. 59° (Chasanowitz and Hell, Ber. 1885, 823; Auwers, *ibid.* 1901, 4266). By treating eugenol with bromine in chloroform at 0°, bromeugenol is formed (Lando, J. Amer. Chem. Soc. 1905, 27, 641). Tribromeugenol and other brom- derivatives (*v.* Lando, *l.c.*; Auwers and Müller, Ber. 1902, 35, 114; Hell and Anwandter, *ibid.* 1895, 2085).

Eugenol methyl ether occurs in several ethereal oils, and can be obtained from veratrol (*v. supra*). It is also obtained by the action of methyl iodide and caustic potash on eugenol (Ciamician and Silber, Ber. 1890, 1164); b.p. 247°–248°. It is readily converted into *iso*eugenol methyl ether, b.p. 263°, which yields methyl vanillin and veratric acid on oxidation with potassium dichromate and sulphuric acid.

***iso*Eugenol**

$(HO)(CH_3O)C_6H_3{\cdot}CH{:}CH{\cdot}CH_3(C_2H_5{:}CH_3O{:}HO=1{:}3{:}4)$ occurs in small quantities in oil of nutmeg (Power and Salway, Chem. Soc. Trans. 1907, 2041), and as the methyl ether in the oil from *Asarum arifolium* (Michx.) (Miller, Arch. Pharm. 240, 371). It is prepared by adding 5 parts of eugenol or an equivalent quantity of oil of cloves to 12·5 parts of potash, dissolved in 18 parts of amyl alcohol, and heating for 16–20 hours at 140°. The product is steam distilled, and the residue acidified with sulphuric acid. The *iso*eugenol separates out, is washed with sodium carbonate solution, and purified by distillation (Tiemann, Ber. 1891, 2870; 1894, 2580; Lairi, Eng. Pat. 17547; J. Soc. Chem. Ind. 1891, 854; Haarmann and Reimer, D. R. P. 57808; Ber. Ref. 1892, 94). The amyl alcohol may be replaced by methyl, ethyl, or butyl alcohols (Gassmann, Compt. rend. 124, 38; F. von Heyden Nachf. D. R. P. 70274; J. Soc. Chem. Ind. 1892, 633). Other methods are to heat eugenol with 4 parts of caustic potash and some water at 220° (Einhorn and Frey, D. R. P. 76982; Frdl. iii. 863; Ber. 1894, 2455); to heat the alkali derivative of eugenol to 200° in the absence of air (Fritzsche, D. R. P. 179948; J. Soc. Chem. Ind. 1907, 1216); and to heat the acid sodium salt of *iso*eugenylphosphoric acid to 150° (*v. Eugenylphosphoric acid*).

*iso*Eugenol forms colourless crystals, m.p. 33°; b.p. 264°–265° (J. Soc. Chem. Ind. 1892, 633), 193·5° (100 mm.), and 266·5°–268·5° (760 mm.); sp.gr. 1·0994 at 4°/4°, 1·0944 at 10°/10°, 1·0872 at 20°/20°; specific magnetic rotation 2·5578; molecular magnetic rotation at 15°, 21·469 (Perkin, Chem. Soc. Trans, 1896, 1247). On oxidation, *iso*eugenol and its derivatives yield the corresponding derivatives of vanillin. Thus *iso*eugenol, when treated with sodium peroxide, yields vanillin itself (Haarmann and Reimer, Eng. Pat. 11952, 14928; J. Soc. Chem. Ind. 1895, 506; 1897, 633; *cf.* Majert, D. R. P. 82924; Ber. Ref. 1895, 878). Ozone oxidises *iso*eugenol in the same way, and vanillin is also produced by the electrolysis of the sodium salt of *iso*eugenol and subsequent addition of acid (Otto and Varley, Amer. Pat. 553039, 553593; Ber. Ref. 1896, 249; *cf.* Otto, Ann. Chim. Phys. 1898, [viii.] 13, 120). Ferric chloride oxidises *iso*eugenol to dehydro*iso*eugenol, m.p. 133° (Cousin and Hérrisey, Compt. rend. 1908, 147, 247).

*iso*Eugenol is readily polymerised by small quantities of mineral acids, acid chlorides, or metallic haloids, forming *diisoeugenol*, which crystallises in colourless needles, m.p. 178° (F. von Heyden Nachf. D. R. P. 70274; J. Soc. Chem. Ind. 1892, 633), 180° (Puxeddu, Gazz. chim. ital. 39, i. 131). Similarly, the ethyl ether of *iso*eugenol, when dissolved in alcohol and treated with hydrogen chloride for some hours, polymerises into diethyldi*iso*eugenol, m.p. 130° (Puxeddu, *l.c.*; Wassermann, Annalen, 179, 375).

The *acyl and aryl derivatives* are obtained by methods similar to those employed for the eugenol compounds, but the solutions must be kept cool to prevent polymerisation taking place; acetyl *iso*eugenol, m.p. 79°–80°; benzoyl *iso*eugenol, m.p. 103°–104°; benzyl *iso*eugenol, m.p. 48° (Pond and Beers, J. Amer. Chem. Soc. 19, 825; Merck, D. R. PP. 103581, 109445; Chem. Zentr. 1899, ii. 927; 1900, ii. 407; Haarmann and Reimer, D. R. P. 57568; Ber. Ref. 1892, 93). If acetyl chloride is added to *iso*eugenol at 54°, and the temperature is finally raised to 80°, diacetyldi*iso*eugenol is obtained, and by hydrolysis with acids, di*iso*eugenol is formed (Tiemann, Ber. 1891, 2870; 1894, 2580). Methylene chloride reacts with an alkaline solution of eugenol forming methylenedi*iso*eugenol, m.p. 50°–52°, which on oxidation yields methylenedivanillin (Lesault & Co., D. R. PP. 75264, 76061; Ber. Ref. 1894, 812, 928).

5-Nitro*iso*eugenol is formed by the action of nitric acid on *iso*eugenol in acetic acid solution; on recrystallisation from *iso*butyl or amyl alcohols it forms a reddish-yellow mass, which decomposes at about 150° (Puxeddu and Comella, Gazz. chim. ital. 1906, 36, ii. 450).

***iso*Eugenol carbonate** is prepared in the same way as eugenol carbonate (*q.v.*) (F. von Heyden Nachf. D. R. P. 61848; Ber. Ref. 1892, 486).

By adding excess of bromine to *iso*eugenol, brom*iso*eugenol dibromide, m.p. 138°–139°, is formed. If only 1 molecule of bromine is added, an unstable *iso*eugenol dibromide, m.p. 95°, is produced. Di- and tri-*iso*eugenol dibromides have been prepared (Hell and Portman, Ber. 1895, 2088; Hell and Bauer, Ber. 1904, 1128; Zincke and Hahn, Annalen, 329, 1).

***iso*Eugenol methyl ether** occurs in the oil of *Asarum arifolium* (*v. supra*). It can be prepared by warming eugenol methyl ether with alcoholic potash (Ciamician and Silber, Ber. 1890, 1165) or by treating *iso*eugenol with dimethyl sulphate and aqueous potash (Mannich, Arch. Pharm. 248, 127); b.p. 263°.

*iso*Eugenol is distinguished from eugenol by the following reactions: (i.) ferric chloride gives an olive-green colouration with its alcoholic solution; (ii.) zinc chloride, a bright rose-pink colour; (iii.) sulphuric acid, a rose-pink colour changing to light-brown.

EUGUFORM, EUMYDRIN, EUPHTHALMIN, EUPORPHIN *v.* SYNTHETIC DRUGS.

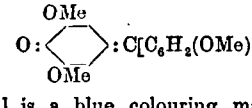
EUPHORBIC ACID, EUPHORBIUM, EUPHORBON *v.* GUM RESINS.

EUPHORINE *v.* SYNTHETIC DRUGS.

EUPHRASIA TANNIN *v.* TANNINS.

EUPHYLLIN. Trade name for a compound of theophylline with ethylene-diamine. A white crystalline soluble powder, used as a diuretic (*v.* SYNTHETIC DRUGS).

EUPITTONIC ACID, *Eupittone, Pittacal, Hexamethoxyaurin* $C_{25}H_{26}O_9$



Pittacal is a blue colouring matter obtained by Reichenbach in 1835 from the high-boiling portions of beechwood tar. Grätzel also from the same products obtained a brown substance which gave the same blue colour reaction with baryta as the pittacal of Reichenbach. The colouring matter, which only exists in small quantity in this brown substance, was extracted and examined by Liebermann (Ber. 9, 334). It is an orange-red crystalline powder, soluble in alcohol and acetic acid, forming brown solutions. It forms with alkalis purple, and with ammonia blue solutions, from which carbon dioxide precipitates blue salts, soluble in pure water. Calcium, magnesium, barium, and tin salts, also give blue precipitates with the alkaline solutions. The calcium and magnesium salts are soluble in pure water. Hydrochloric and sulphuric acids form red solutions, and the latter turns pure blue on warming. In acid solutions, it dyes animal fibres orange, in ammoniacal solution especially with tin mordant, blue-violet. Liebermann called this colouring matter *eupittone*, and regarded it as at least closely allied to pittacal (Ber. 11, 1145). Hofmann (Ber. 12, 1371, 2216), by the action of hexachlorethane C_2Cl_6 on dimethyl pyrogallate mixed with alcoholic potash or soda, obtained a substance identical in composition with the eupittone of Liebermann, and strongly resembling it in properties. It is an orange-yellow substance, soluble in acetic acid, and precipitated therefrom by alcohol. It melts at 200° and decomposes partly into a blue sublimate. It forms the same alkali salts and gives the same sulphuric acid reaction as eupittone. This body is hexamethoxy-rosolic acid $C_{19}H_8(OCH_3)_6O_3$. Heated with alcoholic ammonia, it yields hexamethoxy-rosaniline

$$OH{\cdot}C[C_6H_2(NH_2)(OMe)_2]_3,$$

which crystallises in broad colourless needles, and has no tinctorial properties. When 2 grams eupittone are heated with 20 c.c. alcoholic methylamine (10 p.c.) at 150°–160° for 2½ hours, it yields hexamethoxydimethylformyl*para*leucaniline

$$CH[C_6H_2(OMe)_2NH{\cdot}CH_3]_2C_6H_2(OMe)_2NHCHO$$

m.p. 187° (Liebermann, Ber. 34, 1034). Pyrogallol is produced in attempting to replace the methoxyl groups by hydrogen. Its formation is analogous to that of rosolic acid

$$3C_8H_{10}O_3+CO_2=C_{25}H_{26}O_9+2H_2O.$$

Hofmann terms this body *eupittonic acid*, and uses the name as synonymous with pittacal and eupittone. Eupittonic acid cannot be obtained by heating the sodium derivative of dimethyl pyrogallate or of dimethyl-methyl-pyrogallate separately, in air; a mixture of the two, however, with excess of soda gives sometimes as much as 10 p.c. of its own weight of the acid. The action is comparable with that in which rosaniline is produced from aniline and toluidine.

$$2C_8H_{10}O_3 + C_9H_{12}O_3 = C_{25}H_{26}O_9 + 3H_2.$$

The oxygen necessary to remove the hydrogen is obtained from the atmosphere, as in a closed vessel no such change as the above takes place. Eupittonic acid appears to be dibasic, the sodium and barium salts, $C_{25}H_{24}Na_2O_9$ and $C_{25}H_{24}BaO_9$, have been prepared. Paper steeped in a solution of the acid, and dried, is a most sensitive test for free alkalis on account of the blue colour of the alkaline salts of eupittonic acid. Hydrochloric acid, however, produces the same blue colour. With acetic anhydride, a diacetyl derivative, $C_{25}H_{24}O_9(C_2H_3O)_2$, m.p. 265°, is produced, which, curiously, is insoluble in alkalis, although its molecule ought to contain four hydroxyl groups.

The dibenzoyl derivative $C_{25}H_{24}O_9(C_7H_5O)_2$ forms golden needles, m.p. 232°; the dimethyl ether $C_{25}H_{24}Me_2O_9$ has m.p. 242°; the diethyl-ether $C_{25}H_{24}Et_2O_9$ has m.p. 201°–202°; and the iodo compound $C_{25}H_{26}O_9I_4$ forms brown shining prisms.

Eupittone black, noreupittone, hexaoxyaurin

$C_{19}H_{14}O_7$ or $[C_6H_2(OH)_3]_2C:C_6H_2(OH)_2:O$

is formed by adding eupittone to sulphuric acid at 140° and keeping the temperature at 125° until the mass is pure blue; it is a dark shining black powder, and dyes mordanted fibres through a dirty violet to a deep black; the hydrochloride $C_{19}H_{14}O_7,HCl,C_2H_6O$ is deep blue (Liebermann and Wiedermann, Ber. 34, 1033).

EUPYRIN *v.* SYNTHETIC DRUGS.

EURHODINES, EURHODOLS *v.* AZINES.

EUROBIN. Trade name of a pharmaceutical preparation consisting mainly of the diacetate of chrysarobin (*q.v.*).

EUROPHEN *v.* SYNTHETIC DRUGS.

EUROPIUM. Eu = 152 (*cf.* Urbain and Lacombe, Compt. rend. 1904, 138, 637, and Jantsch, *ibid.* 1908, 146, 473).

Source.—The oxide of this extremely rare element is present in very small amounts in monazite sand, and is extracted from this mineral in the fraction containing the yttrium earths.

Extraction.—In separating europium from its associates, advantage has been taken of the isomorphism existing between the double nitrates of bismuth and those of the metals of the rare earths.

Bismuth nitrate gives rise to a series of double salts having the general formula

$$3M^{II}(NO_3)_2,2Bi(NO_3)_3,24H_2O,$$

where the bivalent metal may be magnesium, zinc, nickel, cobalt, or manganese (Urbain and

Lacombe, Compt. rend. 1903, 137, 568). Magnesium bismuth nitrate

$$3Mg(NO_3)_2,2Bi(NO_3)_3,24H_2O,$$

is isomorphous with the corresponding double magnesium nitrates

$$3Mg(NO_3)_2,2M^{III}(NO_3)_3,24H_2O,$$

where M^{III}=Ce, La, Nd, Pr, Sm, Eu, Gd, and Tb.

To a mixture of these metals in the form of their double magnesium nitrates is added a large excess of magnesium bismuth nitrate. When the product is crystallised methodically from nitric acid solution, the double magnesium nitrates of cerium, lanthanum, praseodymium, neodymium, and samarium first separate, followed by the double salt of bismuth, leaving europium and gadolinium in the mother liquors. As the fractional crystallisation proceeds, the rare earths yielding double nitrates less soluble than the bismuth double salt, are gradually eliminated until at a certain point the middle fractions contain no other tervalent metal than bismuth. When this point is reached, all the samarium has been crystallised out, and thus separated from the europium and gadolinium. The bismuth still in solution is removed from the mother liquor by hydrogen sulphide, and the europium and gadolinium separated by further fractionation of the filtrate, the europium double nitrate being the first to crystallise from this solution (Demarçay, Compt. rend. 1900, 130, 1019, 1469; Urbain and Lacombe, *ibid.* 1904, 138, 627). This crystallisation process is a satisfactory method for obtaining pure europium, samarium, and gadolinium, and affords a means of separating quantitatively europium and samarium (*cf.* Eberhard, Zeitsch. anorg. Chem. 1905, 45, 374).

Europia (*Europium oxide*) Eu_2O_3, obtained from the purified double salt, shows no samarium spectrum, and only the strongest lines of gadolinium (Demarçay, Compt. rend. 1901, 132, 1482); it has a pale pink tint, but when produced by heating the sulphate at 1600°, the colour is somewhat deeper.

Europium sulphate $Eu_2(SO_4)_3,8H_2O$ forms pale-pink crystals, stable in air and dehydrated completely at 375° (Compt. rend. 1904, 138, 627).

The europium salts yield pale-pink solutions and in strong nitric acid they exhibit an absorption spectrum consisting of eight somewhat faint bands.

The spark spectrum is characteristic, and was first observed by Lecoq de Boisbaudran in that given by crude samaria, three very intense lines in the blue being ascribed by him to a new earth Z_ε. The reversion spectrum shows the band λ615 referred by de Boisbaudran to the earth Z_ζ (Compt. rend. 1893, 116, 674; 117, 199).

The most intense lines of the arc spectrum are very characteristic, and constitute a delicate test for europium, which can be thus identified in the crude oxides from monazite after removing the cerium (Eberhard, Zeitsch. anorg. Chem. 1905, 45, 374). The cathode phosphorescence spectrum exhibits the anomalous ray referred by Crookes to the 'meta-element' S_δ. Pure europia, however, gives no phosphorescence spectrum unless diluted with some other earth. With lime in the proportion Eu_2O_3:99CaO, a red phosphorescence is observed, and similar effects are obtained on mixing europia with alumina or gadolinia. Mixtures with excess of the latter give a white, and with excess of europia a red, phosphorescence (Urbain, Compt. rend. 1906, 142, 205, and Seventh Congress of Applied Chemistry, 1909, section 10, 94).

(Ultra-violet and arc spectra, *v.* Exner and Haschek, Sitzungsber. Wien. Akad. 1902, IIa, 3, 42, and Die Wellenlängen der Bogenspektra, 1904.)

Europium has been detected spectroscopically in the sun's chromosphere, in α-Boötis and in β-Geminorum (Lunt, Proc. Roy. Soc. 1907, A, 79, 118). G. T. M.

EUSYNCHITE *v.* VANADIUM.

EUXANTHIC ACID, EUXANTHONE, and EUXANTHONIC ACID *v.* INDIAN YELLOW.

EUXENITE. A rare-earth mineral consisting essentially of columbate and titanate of yttrium and erbium, with smaller amounts of uranium, thorium, cerium earths, iron, &c. Crystals are orthorhombic, but are very rare and indistinctly developed: the mineral is more often massive, with a brownish-black colour and a brilliant pitchy to sub-metallic lustre. In appearance and characters, it closely resembles several of the other rare-earth minerals, particularly polycrase, from which it is not easily distinguished. It is occasionally found in the felspar quarries at several places in the south of Norway (*v.* W. C. Brögger, Die Mineralien der Südnorwegischen Granit-Pegmatitgänge, 1906). Named from εὔξενος, friendly to strangers, in allusion to the several rare earths it contains. L. J. S.

EVAPORATION. The term 'evaporation' is used in connection with technical or manufacturing operations when a liquid is converted into vapour, but in chemical manufactures it is generally limited to those processes where the object is to separate a liquid from a solid which is dissolved in it, or to separate a more volatile from a less volatile liquid. In cases where the liquid to be evaporated is one of the products of the process, and is collected by condensation, the process is known as DISTILLATION (*q.v.*). Where a solid substance contains water, not as water of crystallisation, and without presenting visible moisture or wetness, the process of removing this moisture under suitable circumstances is known as DESICCATION or DRYING (*q.v.*). The operation of evaporation, however, is conducted on the greatest scale in the generation of steam for steam engines, and in the production of steam generally for manufacturing purposes. Although more water is evaporated in connection with the steam engine than for any manufacturing processes, yet great quantities of steam are used as a convenient means of applying and distributing heat, especially when regulated and moderate temperatures are required. In such cases the heat is applied to the vessel to be heated by jacket spaces or through coils of pipes immersed in the liquid to be raised in temperature. Such applications are made in sugar and confectionery manufacture, and in distilleries, breweries, and dyeing, &c.

Water and many other liquids evaporate without the application of heat. A vessel of water freely exposed at the ordinary temperature of the atmosphere soon evaporates and disappears. This is due to the fact that water

vapour has a sensible pressure at ordinary temperatures, and as gases and vapours freely diffuse throughout each other, any water placed with a free surface in a confined space continues to evolve and diffuse its vapour until the pressure of water vapour present in the whole space is at the maximum pressure which corresponds with the temperature. Although evaporation occurs in this way without any application of increased temperature, yet heat is absorbed by the vapour formed from the liquid, and if the evaporation be rapid and be conducted under such circumstances that heat from surrounding objects is prevented from reaching the liquid, then its temperature will be greatly reduced. This fact is illustrated by the well-known lecture experiment of placing a shallow copper cup filled with ether upon a block of wood, and under it a drop of water. When air is blown upon the ether it rapidly evaporates and carries off so much heat from the copper that the water drop under it is frozen and the copper adheres to the wood. A liquid is said to be volatile when its vapour has a considerable pressure at ordinary atmospheric temperatures. At 20°, for example, the pressure of water vapour (or tension as it is somewhat incorrectly called) is 17·39 mm. mercury, whilst the pressure of ether vapour at the same temperature is 433·3 mm. and that of alcohol 44·5 mm. If the liquids be placed in atmospheres whose pressures could be kept at these points by artificial means, then these liquids would boil. As the evaporation under these circumstances is very rapid, relatively to the flow of heat to the liquid from surrounding bodies, if only atmospheric temperature be available, the heat is abstracted so quickly that many liquids freeze.

Advantage is taken of these properties for many purposes in the use of air currents passed over the surfaces of liquids to evaporate them without the application of other than natural heat. Reduced pressures are also applied to evaporate without heating or to reduce the temperature necessary in order to avoid chemical decomposition and also to produce cold mechanically.

Evaporation in steam boilers. The evaporative efficiency of the steam boiler has been more closely studied than that of any other type of evaporating apparatus, and as the principles of the economical application of heat for evaporating are more completely known in this connection, it is advisable to consider it first.

The leading types of steam boilers now in use for the purposes of motive power are as follows: Lancashire, Cornish, Locomotive multitubular, Marine multitubular, and Water-tube or tubulous types.

The Lancashire boiler consists of a horizontal, cylindrical steel or iron shell closed at the ends by flat plates suitably stayed, and having two cylindrical steel or iron flues parallel to each other passing from end to end. These flues serve to receive two furnaces at the front end in which the fuel is burned, and the products of combustion pass through the flues and are conducted round the lower part of the shell through flues arranged in the brickwork setting before they pass to the stack or chimney. Many modifications are made, the principal being in the use of Galloway's conical cross tubes in the flues, and in running both tubes into a common combustion chamber.

These boilers are extensively adopted for large stationary engines used for driving spinning mills and factories. The standard size is 30 feet by 7 feet diameter, with internal flues each 2 feet 9 inches diameter. The firegrates are generally 6 feet long. As the temperature at which the hot gases enter the stack is higher than is desirable, a heat-absorbing apparatus known as an *Economiser* is generally added. It consists of a series of vertical cast-iron pipes, suitably connected together, through which the cold feed water is pumped in the opposite direction to the flow of the burned gases around the exterior, so that the water is gradually heated as it passes along the pipes, and the gases as they cool come in contact with cooler water. By this arrangement a considerable addition is made to the heat absorbed by the water.

The following test of the evaporation efficiency of a pair of ordinary Lancashire boilers, with and without economisers, was made by Longridge.

The two boilers were each 30 feet long by 7 feet in diameter, with internal flues of 2 feet 9 inches diameter, having five Galloway's cross tubes in each. The firegrates were 6 feet long, and boilers were housed and the tops covered with brick. The economiser had 80 tubes in 16 rows. The heating surface of the boilers was 1870 square feet; heating surface of the economiser, 800 square feet; total surface, 2670 square feet. The grate surface was 66 square feet, and the average steam pressure by steam gauges 83 lbs. per square inch above atmosphere.

Longridge found, as the result of a 7½ hours' trial, that 1 lb. of fuel under the actual conditions evaporated 9·66 lbs. of water, but, allowing for moisture in the coal, 9·82 lbs. of water were evaporated by each pound of dry fuel.

The calorific value of 1 lb. of dry fuel used was 13,363 British thermal units. The coal was Arley Mine, from Abram Colliery, Wigan. The total weight of gas, air, and water vapour per pound of dry fuel passing through the furnaces, was 15·8 lbs.

These figures give the combined efficiency of boilers and economisers as 78·4 p.c., that is, out of 100 heat units placed upon the firegrate, 78·4 were utilised for the intended purpose, that of raising steam, and 21·6 were employed in other ways, producing draught, drying fuel, losses by radiation, and unburned or partly burned fuel. Of this 78·4 p.c. utilised in evaporation, 71·6 was due to the boiler alone, and the remaining 6·8 p.c. was due to the economiser.

The following shows the disposal of 100 heat units placed upon the fire bars in the form of fuel, in the boilers only:—

Heat used in evaporating water .	71·57
Heat contained in products of combustion and excess air and vapour accompanying them . . .	17·81
Heat lost in evaporating moisture in coal	0·13
Heat lost by imperfect combustion .	0·00
Heat lost by unburned combustible falling through firegrate with ashes	4·28
Heat lost in drawing ash and clinker	0·36
Difference, radiation, and losses unaccounted for	5·85
	100·00

One hundred heat units given to the economiser were disposed of as follows :—

Heat used in evaporating water .	38·12
Heat contained in chimney gases .	58·12
Loss by radiation, &c. . .	3·76
	100·00

One hundred heat units put upon the firegrate in the form of fuel were disposed of by the combined apparatus as follows :—

Heat used in evaporating water .	78·38
Heat lost in chimney gases . .	10·35
Heat lost in evaporating moisture in coal and lost carbon . .	4·75
Difference, radiation, &c. . .	6·52
	100·00

In these trials the total fuel burned per hour was 1090 lbs. or, deducting moisture 1072·72, and the water evaporated per square foot of total heating surface per hour was 3·94 lbs., or per square foot of boiler heating surface 5·63 lbs. per hour.

The total feed water to the boiler per hour was 10,533 lbs. The water-level surface in the boiler was 390 square feet, and the total evaporated per square foot of that surface was 27 lbs. water per hour.

As an average of many tests, the evaporative efficiency of an ordinary Lancashire boiler of good construction with a Green's economiser may be taken as 80 p.c. in ordinary work with careful firing.

The Cornish boiler is a cylindrical shell with flat ends like the Lancashire, but as it has only one internal flue, its evaporative efficiency is inferior to that of the Lancashire.

The locomotive multitubular type of boiler consists essentially of a rectangular firebox containing the furnace surrounded by water, having its flat surfaces suitably stayed and riveted to a cylindrical shell through which pass a great number of metal tubes. The water surrounds these tubes, and the products of combustion pass through their interior and are discharged into the smokebox and thence pass away by the chimney. In a locomotive the draught is created by the exhaust steam blast discharged up the chimney. The advantage of these boilers is their enormous power of producing steam in small bulk and weight, but they are not so economical of fuel as the stationary type. A common efficiency is 71 p.c., but with care and well-designed feed-water heater arrangements, even in small boilers of this type an efficiency may be got as high as that obtained by Lancashire boilers with economisers. In the Society of Arts' trial, published in their journal in 1889, a boiler of this kind with a feed-water heater in the smokebox gave an evaporative efficiency of 82 p.c., that is, 82 p.c. of all the heat placed upon the fire in the form of fuel was applied to its intended work of producing steam. These tests were most carefully conducted, and analysis made of fuel and escaping products to trace the disposal of all the heat. Only 10·5 p.c. of the total heat was lost in the heat of the furnace gases, and 9·0 was estimated as loss by radiation. This figure cannot be taken, however, as the value given in ordinary work, as the trial was most carefully made, and the whole conduct of the machinery was under the direct supervision of the highest skill to be found in the works of the makers.

The standard *marine multitubular type* of boiler consists of a cylindrical shell of relatively great diameter, with cylindrical flues containing the furnace, and the products of combustion return through numerous tubes before discharge up the funnel.

The evaporative efficiency of such boilers is not so high as either the Lancashire or the locomotive type. Careful trials have been made by a research committee of the Institute of Mechanical Engineers, consisting of many leading engineers, on board the s.s. *Meteor*. The trial lasted 14 hours, the consumption of fuel was 4005 lbs. per hour, and the total evaporation 29,860 lbs. per hour, the heat accounted for in the steam evaporated amounting to 62 p.c. In boilers of this class it is unusual to have feed-water heaters or economisers. Mr. Ebenezer Kemp, of Glasgow, has fitted several steamers with compound boilers, or boilers to which large feed-water heaters or economisers were applied, with good results.

The following gives the main details of the set fitted on board the s.s. *Caloric*. The high-temperature boiler was single ended, 12 feet diameter and 11 feet 6 inches long, having two furnaces 3 feet 9 inches diameter, and a total heating surface of 1613 square feet. There were four multitubular feed-water heaters or low-temperature boilers, as Mr. Kemp calls them, 4 feet 6 inches in diameter by 8 feet 4 inches long, with a total heating surface of 3505 square feet. That is, the feed-water heater had rather more than double the heating surface of the boiler proper. The arrangement gives a saving of 15 p.c. as compared with ordinary marine boilers.

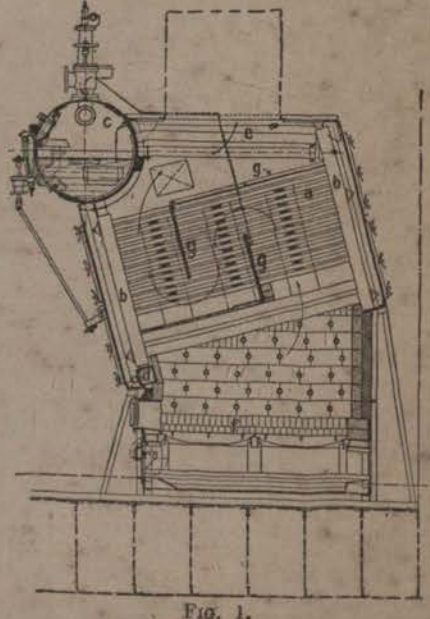


FIG. 1.

The *water tube or tubulous* type of boiler differs from the tubular in containing the water

in the interior of the tubes, and allowing the furnace gases to play upon the exterior.

This type of boiler is now largely used for stationary engines, and also for marine purposes. The forms mostly used are those manufactured by Messrs. Babcock and Wilcox, and by Messrs. Yarrow. The Babcock and Wilcox marine type of boiler (illustrated at Fig. 1) consists of an arrangement of inclined tubes *a*, forming the bulk of the heating surface, the tubes being arranged in sections and expanded at both ends into wrought-steel boxes or headers, which are in connection with a horizontal steam and water drum *c*, and a mud drum *d*. By means of the connections *e*, *e* with the steam and water drum at the high ends of the headers, the steam generated in the tubes is liberated, and water supplied to take its place. The firegrate *f* is underneath the nest of tubes, and the hot gases, as shown by the direction of the arrows, come into intimate contact with the whole of the heating surface, baffle plates *g* being provided to direct the gases. The furnace is lined with firebricks or with firetiles bolted to the side plates, and the whole boiler is enclosed in an iron casing, fitted with refractory material preventing radiation of heat.

The steam generated in the tubes rises vertically through the rear headers into the steam and water drum, from which the water returns to the front headers and the tubes, so that there is a continuous circulation of water in one direction. The feed water enters the steam drum below the water level, passing vertically through a feed nozzle into the steam space, and is deflected downwards by a cover or guard into the water space. This type of boiler is capable of evaporating about 12·3 lbs. of water from and at 212°F. per lb. of coal burned, at a coal consumption of about 20 lbs. per square foot of grate area per hour.

In the Yarrow type of water-tube boiler, illustrated by Fig. 2, the heating surface consists for the most part of a large number of small

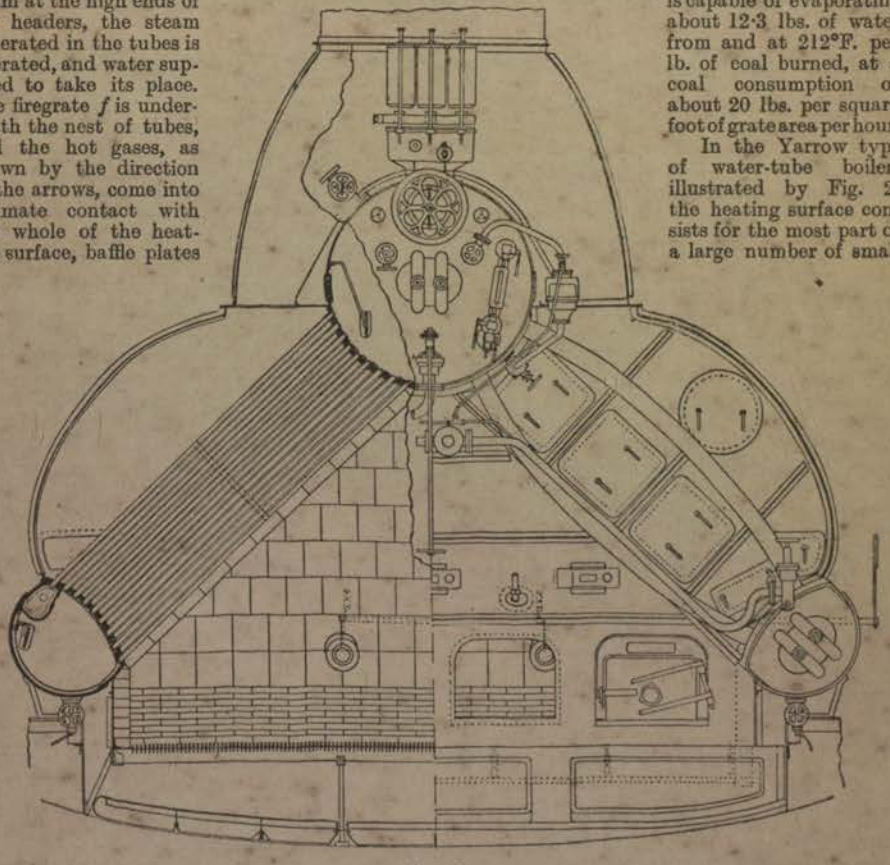


Fig. 2.

inclined tubes leading from two horizontal water drums situated at the bottom of the boiler, to a horizontal steam drum situated at the top. The ends of the tubes are expanded into apertures in the drums. The two outer rows of tubes lead from a space, partitioned off from the water drum, to the steam drum, and the feed water is delivered into this space. The steam is taken off by a pipe from the top of the steam drum. The firegrate is situated below the tubes, and the gases pass through between the tubes, being prevented from going straight up the chimney by baffle plates. This boiler is capable of evaporating from 11·4 to 12·96 lbs. of water from and at 212°F. per lb. of coal burned, the larger figure being obtained when the rate of coal consumption is 12·65 lbs. per square foot of grate area, and the smaller figure with a rate of consumption of 60·6 lbs. per square foot of grate area.

Both these types of water-tube boiler are very largely used by the Admiralty on modern battleships and cruisers. On smaller vessels, a smaller type of Yarrow boiler, and the White-Forster water-tube boiler, are very generally used. The White-Forster differs from the

Yarrow mainly in the form of the tubes, and in employing a larger steam drum in relation to the size of the boiler.

In recent years, a type of steam boiler, known as the flash boiler or generator, has come into use, where very rapid steam raising and small size of boiler are required, as in steam-propelled motor vehicles. The best-known form of this type of steam generator is the White generator, fitted to the White steam car. This generator is shown at Fig. 3. It consists of

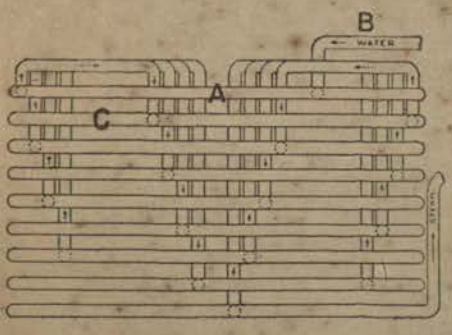


FIG. 3.

nine coils of steel tubing placed one above the other, and connected in series. The water is introduced into the top coil A by a pipe, B, and thence passes upwards and down to the second coil C, and so on downwards through the generator. As the water has to rise to the level of the top of the boiler, in passing from coil to coil, gravity can have no effect on its descent through the boiler, so that the circulation is dependent entirely upon the action of the pumps. The water is pumped into the upper coil, and steam issues from the lower coil. The point at which the water 'flashes' into steam is dependent on the different running conditions. Owing to the very small capacity of the generator—less than one-third of a cubic foot—steam can be very quickly raised. The fuel, which is in the form of vapour, is supplied under pressure to a burner placed below the generator.

Evaporation in open vessels. In many chemical manufactures it is necessary to evaporate off water in which the substance, the object of the process, is dissolved, and in such cases, when heat is to be applied, it is desirable to economise fuel to the greatest possible extent. The heat of waste gases is therefore used as much as possible. The method of applying heat varies considerably with the chemical nature of the substance dealt with, and choice of economical apparatus is often limited by the corrosive nature of the liquid to be evaporated. In the process of concentrating oil of vitriol from the dilute acid, a series of shallow open lead pans receives the diluted acid and heat is applied below. The hot furnace gases are allowed to impinge upon the bottom of the vessel containing the weakest acid, and therefore requiring the greatest quantity of heat for evaporation, and as the gases cool they impinge upon the succeeding vessels of stronger and stronger acid, requiring less quantity of heat until the acid has become as concentrated as it is safe to trust to leaden vessels. It is then run into the platinum pan for its final concentration. Instead of this plan, in some cases the furnace gases are passed over the surface of the acid in order to heat it from above, and the volume of gases in motion removes the vapour as fast as it is formed. The advantage of surface evaporation arises not from the fact of its being economical, because liquids are heated with difficulty from above. The hot liquid in contact with the gases expands and has no tendency to cause convection currents, but rather remains stationary above the colder portions, and accordingly it is always advisable to heat from below when possible. In many processes, however, during evaporation, a deposit comes down, and this, coating the bottom of the vessel, prevents the free contact of the metal with the liquid. The resistance to the passage of heat from the metal to the liquid is thereby much increased, and the bottom suffers rapid destruction from over-heating. In boilers using very hard water this is a fruitful source of trouble and danger.

When surface evaporation is resorted to, large surfaces are exposed in shallow tanks over which the flame and hot gases from a furnace are allowed to pass. The pans are covered in so that the radiant heat from the brickwork assists the action of the flame and hot gases. Arrangements of this kind are used in evaporating weak alum liquors, and the tanks are built up of bricks bound together with a cement composed of lime and alum shale. Sometimes an open pan is placed above the gases to contain the feed liquid and heat it in its progress to the evaporating pans.

Evaporation of brine. Brine is sometimes evaporated by allowing the liquor from the springs to flow over masses of twigs in such a manner as to expose very extensive surfaces to the action of air currents; by pumping over a succession of these surfaces it is gradually concentrated. When artificial heat is applied to the evaporation of brine, large shallow salt pans are used. They consist of flat quadrangular vessels of plate iron supported upon suitable brick walls, forming flues which distribute the heat from furnaces placed in the centre part under the vessel. The flames strike directly upon the bottom of the vessel, and the hot products of combustion are conducted outwards by flues leading to the stack or chimney. In this way they traverse the whole bottom surface of the evaporating pans. The pans are of great area, often 60 feet long by 30 feet wide. The water vapour is collected by a large conical hood and carried off by a separate chimney. The sides of the lower part of the cone are so constructed that they can be opened to admit air from the direction in which the wind is blowing. This assists the evaporation by carrying off the water vapour generated and exposing the surface to a continual air current.

If heat enough to cause a liquid to boil be applied, an air current will not increase the evaporation, but will tend to diminish it by cooling the vessel containing the liquid; but when the liquid does not reach the boiling-point, the continuous removal of the atmosphere in contact with the liquid is necessary. If this be not done, then, so soon as the atmosphere has become saturated with the vapour, that is, so

soon as the water vapour is present in quantity sufficient to produce the pressure which corresponds with the temperature of the liquid, the evaporation ceases.

It is a necessary condition of evaporation at temperatures less than the boiling-point, that the atmosphere into which the evaporation takes place should be continuously renewed, and it is advisable that the air into which the water evaporates should not be of lower temperature than the liquid. When the temperature of the air is lower than that of the liquid, the volume of vapour carried off is much reduced, as the air must be heated by the vapour before it is capable of carrying off the volume equivalent to the vapour pressure. Producer gas is used for evaporating the brine at Ischl salt works, and the operation is conducted in deep rectangular plate-iron vessels grouped together, and fed continuously by a system of distributing pipes.

Steam is much used to supply the heat required for evaporation, especially when the substances to be dealt with are of an easily decomposable nature if overheated. The heat is often applied to the vessel by means of a steam jacket, that is, the vessel is made double walled, and the interspace is utilised to receive the hot steam. When the temperature requires to be higher than 100°, the jacket space is constructed to withstand pressure, and steam under boiler pressure is supplied, but steam is most commonly used at atmospheric pressure and applied to the liquid by passing through rows or coils of pipes immersed in it. The arrangement of these pipes varies, and in some cases they are so connected as to be capable of hingeing out of the vessels for ready access and cleaning purposes.

Milk is now rapidly evaporated by spraying into heated air without raising the milk temperature to such a point as would cause chemical change.

Evaporation under reduced pressures. In the older processes of sugar manufacture, the sugar liquors were concentrated by the direct application of heat from a fire upon the vessels containing them, but the greatest difficulty was experienced in preventing decomposition when the solution became concentrated. To avoid this difficulty, the vacuum pan was introduced by Howard, and in various modified forms it is still used. The boiling-point of a liquid depends upon the pressure to which it is subjected, and by reducing the pressure the boiling-point is greatly reduced. The vacuum pan consists essentially of a globular copper vessel containing the sugar liquor, and having the lower portion steam jacketed, while steam also passes through a coil of pipe immersed in the liquid. The upper part of the vacuum pan carries a circular steam dome or cylinder from which a pipe passes to a vessel intended to collect any liquor which may have primed over. From this vessel it is run back into the pan again. An air pump exhausts the apparatus and passes the steam to a condenser of usual construction. Fig. 4 shows a vacuum pan made by Messrs. Manlove, Alliot, & Co. The vacuum pan A is formed in two portions and bolted together. It is fed with liquor from the vessel B by suitable cocks, the pipe connections *a*, *b* being arranged to equalise the pressure within the vessel, so that the flow may be towards A. The live steam is admitted at the valve C, and passes through coil D into the jacket E, from whence it discharges and drains by the pipe F. The cylindrical dome or cylinder G prevents any great priming, but any liquid which may find its way by the pipe H is caught in the cylinder I and returned to A by the pipe K. The pipe L leads to the air pump and condenser. A thermometer placed in the upper part of the pan indicates the temperature of the operation, whilst a vacuum gauge or barometer column is

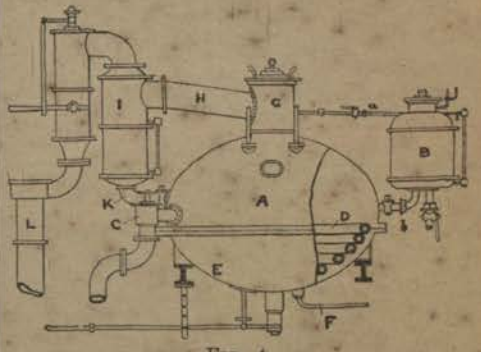


FIG. 4.

used to show the pressure within. The boiling-point of the liquid at atmospheric pressure is about 250°F., and this is reduced to 150°F. by using the vacuum pan.

Fig. 5 shows a vacuum pan of modern construction, made by the Mirrlees Watson Co., Ltd., of Glasgow. In this vacuum pan, the liquor is heated in the vessel *a* by coiled steam pipes *b*, and also by reason of its passing upwards through small tubes *c*, through a steam chamber, *d*, the down flow of the liquor taking place through the central large tube *e*. In other respects, the operation of this vacuum pan is similar to that shown in Fig. 4.

Evaporation under reduced pressure by triple and multiple effect. It is evident that as a liquor becomes more concentrated the boiling-point rises, and in evaporating liquids liable to chemical change by overheating, the pressures under which boiling is effected must be arranged to keep the temperature within safe limits. In the case of sugar liquor this safe limit is 227°F. Steam at 5 lbs. per square inch above atmosphere has this temperature, and if it be applied to a pan containing a weak sugar liquor at atmospheric pressure, the liquor will boil.

Neglecting losses by radiation and like causes, the steam coming from it has the same amount of heat as was imparted to the liquor by the steam under slight pressure, and if it be conducted to the coil and jacket of a second pan in which a slight vacuum is maintained, it will generate almost its own weight of steam at lower pressure and temperature, and so evaporate the water from the second pan. If the steam so generated be taken to the coil and jacket of a third pan, its heat can again be utilised to evaporate the liquor there, provided the vacuum is sufficient to allow it to boil. This process may be continued until the original heat of the steam supplied to the first pan is dissipated by conduction and radiation. This is the principle of the 'triple-effect' apparatus, by which a great

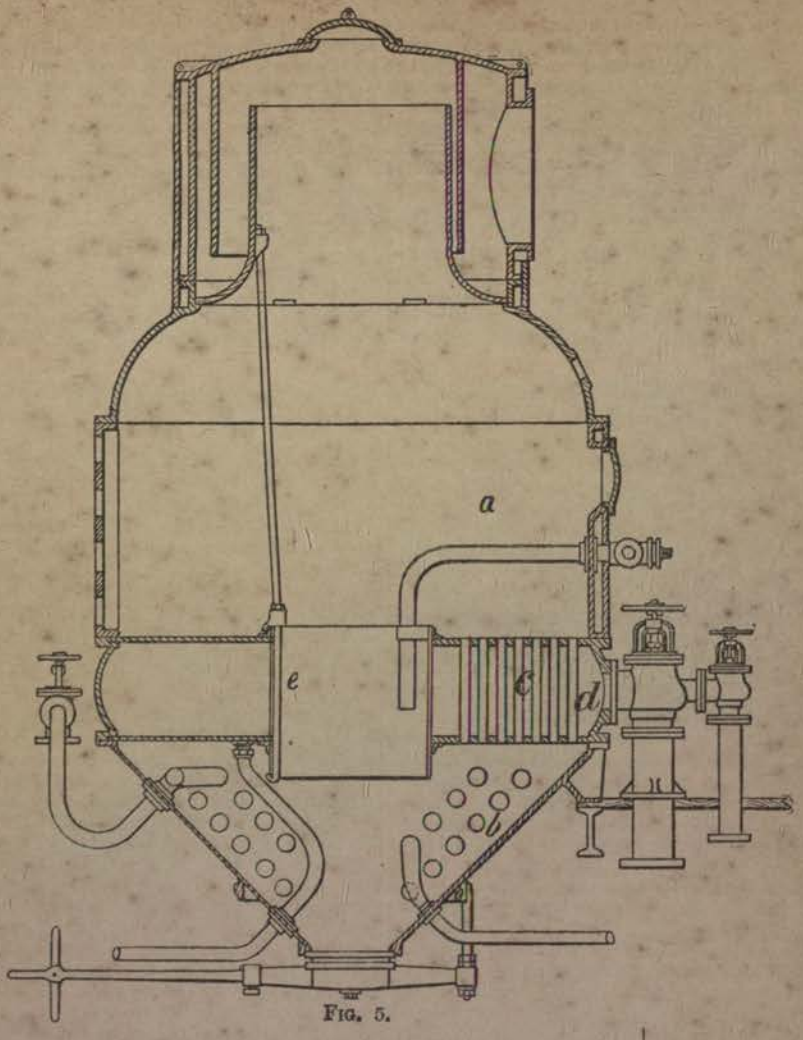


FIG. 5.

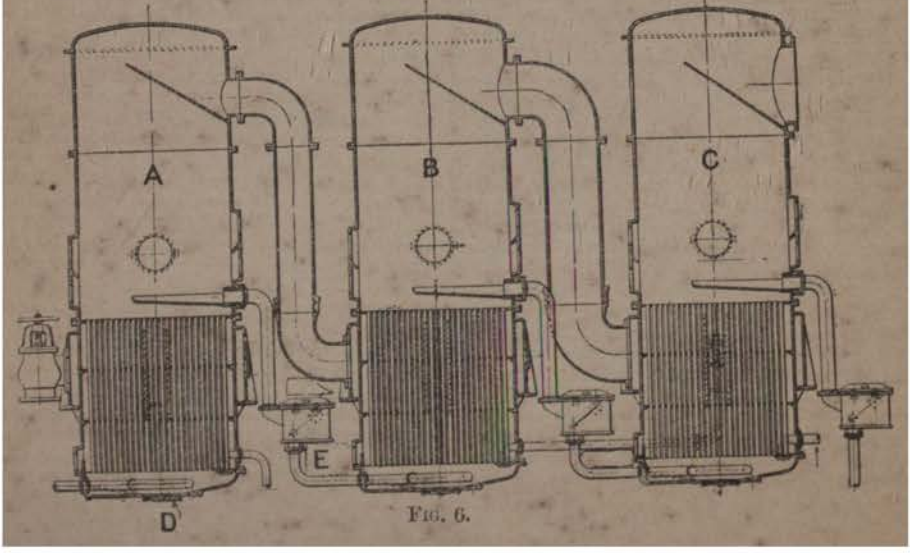


FIG. 6.

economy is effected in the amount of fuel needed to evaporate a given weight of liquor. The steam from one pan at higher pressure proceeds to the coil and jacket of the next, and the steam from the second proceeds to the coil and jacket of the third, the pressures within the pans proceeding in descending order as well as the temperatures.

Fig. 6 is an illustration of a triple-effect evaporator of the 'Hagemann' type, constructed by the Mirrlees Watson Co., Ltd., for concentrating sugar. In this evaporator, the liquor is fed through an internal perforated pipe D at the bottom of the vessel A, and the flow of liquid from vessel to vessel is automatically regulated by traps E, the liquor passing through the vessels A, B, and C in turn, the reduction in pressure being so arranged that it is least in A, more considerable in B, and greatest of all in C, so that the boiling-points are lower in each succeeding vessel. The heating surface is obtained by means of a number of vertical tubes F, through which the liquor passes, these tubes being arranged in a steam space divided by horizontal partitions G. The steam enters the steam space at the top above the upper partition, and passes to the intermediate space through apertures in the partition, slightly larger than the tubes which pass through them, the rush of steam through the openings removing the water of condensation from the surface of the tubes, and improving their efficiency.

The Yaryan evaporator. This ingenious evaporator is the invention of H. T. Yaryan, of Ohio, U.S.A., and it is now largely used in this country, the Continent, and America. It utilises evaporation under reduced pressures as with the triple effect and also multiple effect. It differs from other inventions of the same class in the method of applying heat to the liquid to be evaporated, whereby the liquid is heated in small quantities at a time, and is brought into very effective contact with the heating surfaces. Instead of using coils immersed in a liquid which is also heated by jacketed surfaces, the heat is applied by steam to the exterior surfaces of tubes, and the liquid to be evaporated is pumped within these tubes. The tubes are arranged in straight cylindrical drums, and pass from end to end, terminating in chambers with partitions so placed that when the liquid is pumped in at one end of a series it must pass through the whole series before escaping into the separating chamber. Fig. 7 is a section of one drum of the evaporator, showing that the liquid is pumped in at one end, travels along in the direction of the arrows, and finally escapes with the steam which is generated into the separator. The tubes are divided into sections termed 'coils,' and each section consists of fine tubes coupled at the ends so as to form a continuous passage. The liquid and vapour pass from section to section in series, and so come into effective contact with the whole surface. As the liquid is pumped in it evaporates, and the steam produced carries it forward through the tubes, so that a mass of liquid and steam is brought in contact with every part of the whole heating surface, moving at a high velocity because of the steam generated, which has only the one direction of escape, that is, through the whole system of tubes in each towards the separator. On issuing from the last tube, the steam fills the separator and escapes by a pipe shown in the direction of the arrow, while the liquid falls to the bottom as shown, and drains off to the collecting chamber. The steam is

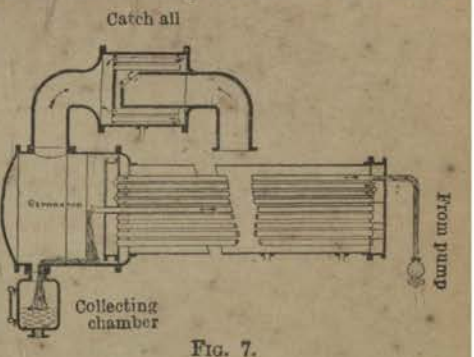


FIG. 7.

further separated from any liquid which may form or prime over, in a vessel termed a *catch all*. This consists of a cylinder having a perforated plate carrying a number of tubes through which the steam passes and impinges upon the end of the vessel, and so deposits any liquid it may carry, which drains off by a pipe to the collecting vessel, while the steam discharges into another pipe as shown by the arrows. This steam heats the second vessel, and the steam from the second heats the third, and so on. The advantages of this apparatus are greatly increased efficiency of heating surface and a rapid and compulsory circulation. Only a small quantity of liquid is in the apparatus at one time, and so it is exposed to heat for a much shorter period than in the ordinary vacuum pan, which is an important point. The apparatus avoids entirely the inversion of sugar which always occurs to some extent in the older vacuum pans because of the long period of time taken to evaporate the large quantity of liquid they contain, amounting in some cases to thousands of gallons. The Yaryan evaporator can be started very rapidly, as it contains but a small mass to be heated. At the same time, the details are arranged to permit of ready access to the tubes and ready cleaning. This is greatly assisted by the fact that the tubes are straight. Fig. 8 is a general external view of a triple-effect apparatus upon this principle, showing the feed and exhausting pumps as well as the various pipe connections and intermediate receivers.

According to the patentees of the Yaryan apparatus, their double effect will evaporate 16 lbs. of water for every pound of coal consumed under the boiler, 23½ lbs. in a triple effect, 30½ lbs. in a quadruple effect, assuming that the boiler is so constructed as to evaporate 8½ lbs. of water per pound of coal. The ordinary performance of a single vacuum pan is only 8½ lbs. of water evaporation per pound of coal.

The Yaryan apparatus has, since its first introduction in 1888, been greatly improved in design and efficiency, and large sextuple-effect apparatus working on the Yaryan principle have been constructed by the Mirrlees Watson Co., Ltd., for distilling water, and also for use in the

Solvay process of soda manufacture in Europe and America. Fig. 9 shows this apparatus arranged as an evaporator for the concentration of 600,000 kilos. of caustic soda liquor per day of 24 hours from 16° to 30°Beaumé, equivalent to an evaporation of 300 tons of water per day. In this evaporator there are six external heaters, through each of which the water of condensation passes, and thus, by gradual increments, the temperature of the feed liquor is raised in its passage from the sixth to the first heater, to approximately the temperature

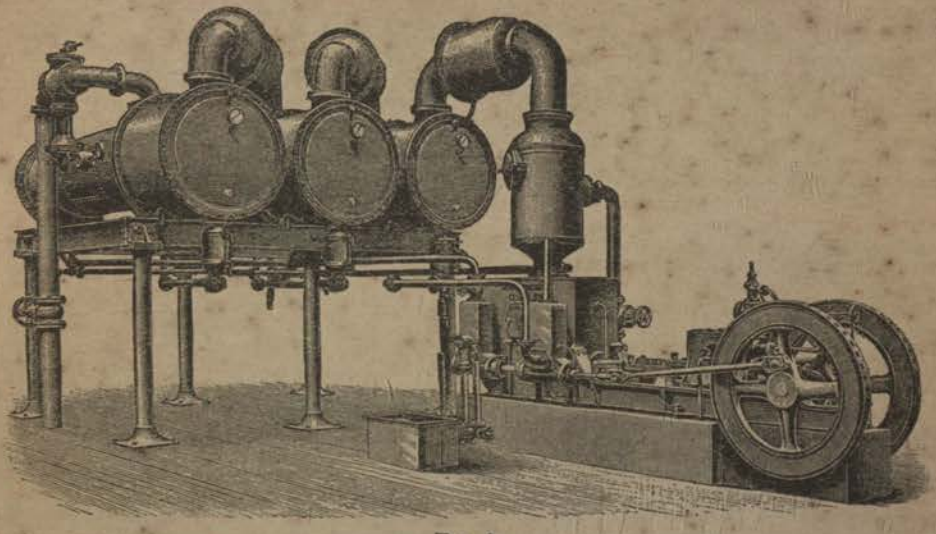


FIG. 8.

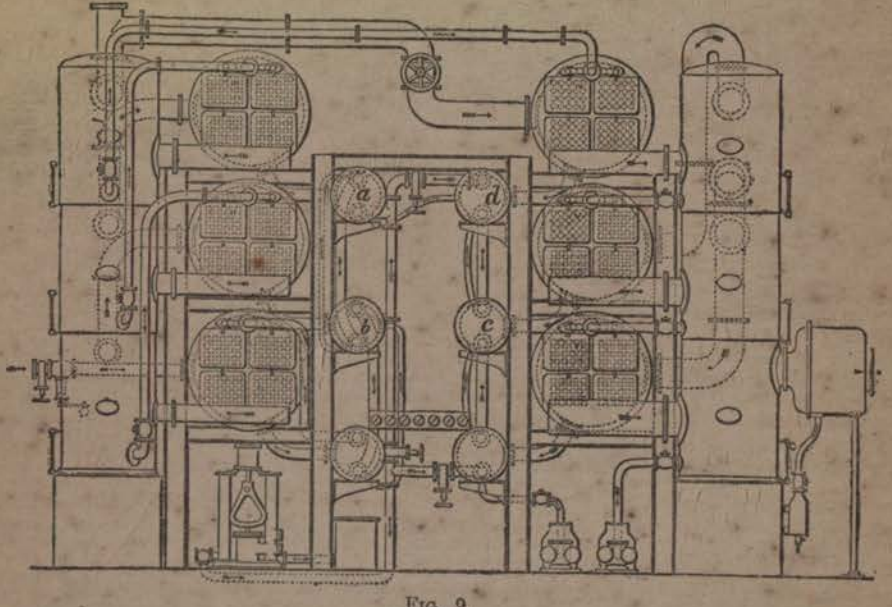


FIG. 9.

obtaining in the shell of the first effect. The flow in the various parts of the apparatus is indicated by arrows in the figure. In this type of apparatus, the liquor to be concentrated enters the distribution header at the top of each effect, and the liquor and vapour pass to the separator from the bottom, so that the liquor in its passage through the tubes forms a film on the surface.

Evaporation in mechanical refrigerators. A separate class of mechanical refrigerators exist in which the cooling or refrigerating effect is produced by evaporation. Liquids used are ether, anhydrous ammonia, and anhydrous sulphur dioxide. In all of these the process of the machine is identical. The volatile liquid is introduced into a chamber at a pressure at

which it is liquid, and the vapour is rapidly withdrawn from the vessel by a pump. The rapid evaporation absorbs heat so quickly that the temperature falls and a brine or other liquid is cooled within a coil of pipes immersed in the liquid. By circulating this brine, the low temperature may be utilised for reducing the temperature of a cold store room or for producing ice.

The vapour drawn off by the pump is compressed and cooled by passing through tubes surrounded by water, and so becomes liquid again. It is then injected into the evaporating chamber again, so that the process is practically continuous, and but slight renewal of the volatile liquid is necessary to make up for small leakages.

The same principle is applied in Carre's freezing machine for freezing water. In this case the vapour is removed from the surface of the water by a pump and condensed by strong sulphuric acid. Ammonia is also utilised in another apparatus in solution in water for the same purpose. By alternate expulsion from the water and absorption, cold is obtained.

The rapid evaporation of liquid carbonic acid, air, and other bodies which are gaseous at normal temperatures and pressures, has also been used to produce low temperatures for liquefying the more permanent gases. D. C.

EVERNIC ACID and EVERNINIC ACID. Evernic acid or *lecanoric acid monomethyl ether*, was first isolated by Stenhouse from the *Evernia prunasti* (Annalen, 68, 83), and has been found also by Hesse (Ber. 1897, 30, 366) to exist in the *Ramalina pollinaria* (comp. also Zopf, Annalen, 1897, 297, 271).

The lichen is extracted with diluted milk of lime, the extract neutralised with acid, the precipitate collected, dried, and digested with a little boiling alcohol. The hot alcoholic liquid, treated with its own volume of water, deposits crystals of evernic acid (Stenhouse).

Evernic acid crystallises in small colourless needles, m.p. 168°–169°, readily soluble in hot alcohol, and when boiled with solutions of the alkali hydrates or baryta water, gives CO_2, orcinol, and everninic acid

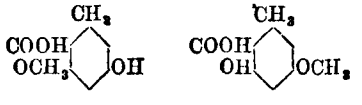
$$C_{17}H_{16}O_7+H_2O=C_9H_{10}O_4+C_7H_8O_2+CO_2.$$

Ramalic acid suffers a similar decomposition.

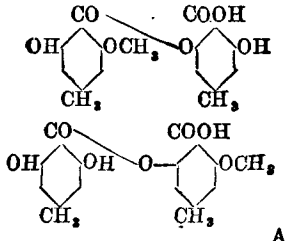
Everninic acid (orsellinic acid monomethyl ether) resembles benzoic acid in appearance, melts at 157°, and yields the ethyl ester

$$C_9H_9O_4(C_2H_5),$$

m.p. 72°. By digestion with hydriodic acid, everninic acid gives orcinol, CO_2 and one molecule of methyl iodide. According to Heinrich (Ber. 1904, 37, 1406), two formulæ are possible for orsellinic acid :—



Hesse's expression (J. pr. chem. [ii.] 57, 253) of the isomerism of evernic acid and ramalic acid, given below, and which is based upon the older formula of orsellinic acid, apparently therefore requires revision.



A. G. P.

EVERNIIN *v.* GUMS.

EVODIA MELIÆFOLIA. This tree, belonging to the *Rutaceæ*, is found in China and Japan, where its bark is largely employed in dyeing and in medicine. It was formerly described by Loureiro as *Pterocarpus flavus*, but this error was eventually corrected by P. W. Squire (Pharm. J. [3] 1888, 18, 785), who showed it to be really *Evodia glauca*, which is synonymous with *E. meliæfolia*. By qualitative tests, Martin, Tokio (Arch. Pharm. 1878, 13, 337) and Squire (*l.c.*) suspected the presence of *berberine*, and this colouring matter was subsequently isolated by Perkin and Hummel (Chem. Soc. Trans. 67, 415). A. G. P.

EXALGIN. Trade name for methyl acetanilide (*v.* SYNTHETIC DRUGS).

EXODIN *v.* SYNTHETIC DRUGS.

EXPLOSION OF GASEOUS MIXTURES. Within recent years there has been an enormous increase in the extent to which the internal combustion engine has been utilised, and there are now many millions of h.p. at work on this principle. Gas engines using coal gas, producer gas, or blast-furnace gas, are now working for all powers up to and above 1000 h.p. per cylinder, and a large number of heavy oil engines are also in use. In addition there are over two million h.p. of petrol motors at work.

In internal-combustion engines working on the constant volume cycle, the motive power is produced by the explosion of mixtures of inflammable gas or vapour and air in certain proportions, and the pressure produced by the explosion is utilised to propel the piston of an engine, as is done by the steam pressure in a steam engine.

In order to understand the phenomena which take place in the actual engine, it is desirable first to consider simple gaseous explosions.

Explosion of mixtures of hydrogen and oxygen and of hydrogen and air.—When a true explosive mixture of hydrogen and oxygen (2 vols. H and 1 vol. O) is confined within a closed vessel at atmospheric pressure and temperature, and it is fired by the electric spark or other means of ignition, the pressure rises rapidly to a maximum of about 10 atmospheres; that is, the pressure rises from 1 to 10 atmospheres, an increase of 9 atmospheres.

This increase of pressure at constant volume is entirely due to the intense heat of the chemical combination of the two gases, and notwithstanding the contraction of volume caused by the formation of steam gas, the temperature of the steam formed is so great that high pressure is produced.

If the explosion vessel be considered as an air

thermometer, and the change of pressure as an indication of increase of temperature of a constant volume of permanent gas, then the temperature is very easily arrived at; thus, taking the temperature of the gases before explosion as 5° (Bunsen's experiments), an increase to 10 atmospheres means that the absolute temperature rises from 273+5=278° to 278×10=2780° or 2507°; but it is impossible to assume no contraction, for in that case there would be no combination. If complete combination at the moment of maximum pressure be assumed, then the effect upon the measurement of temperature is the same as if in an air thermometer one-third of the whole volume had been abstracted during heating, that is, the pressure of steam gas, reduced to 5° and assuming no condensation, would be only $\frac{2}{3}$ atmosphere. In which case 10 atmospheres pressure means $10/\frac{2}{3} = 15$ times the original temperature, or 278×15=4170°, corresponding to 3897°.

Calculating from the known amount of heat evolved by the combination, and assuming the specific heat of steam at constant volume to be 0·37 for high as well as low temperatures, then the maximum temperature of the explosion should be about 9000°, assuming complete combination previous to maximum pressure and no loss of heat while attaining it. As Bunsen proved that maximum pressure was attained in his experiments in $\frac{1}{3000}$ of a second, and that the high temperature succeeding lasted at least $\frac{1}{50}$ of a second, any loss of heat while rising may, for the present, be disregarded.

Owing to the contraction in volume on combustion of the gases mostly used in gaseous explosions, the explosion vessel cannot be considered as an air thermometer, and for this reason, without knowing the amount of combination, it is impossible to accurately estimate the temperature from the maximum pressure reached in the experiment, but it may be stated with confidence that it is higher than 2500° and lower than 3900°, and it is certain that maximum temperature attained does not nearly account for the amount of heat evolved. Either, then, neglecting heat loss on explosion, combination is incomplete, or, if complete, some change in the capacity for heat of the gases present has occurred.

With a mixture of 2 vols. H, 1 vol. O, and 3·75 vols. N, at an initial temperature of 10°, Bunsen obtained an explosion pressure of 7·5 atmospheres. On assumption of no contraction, this corresponds to 1849°; assuming complete contraction, it is 2220°. Here the range of error is less, as the diluting nitrogen does not contract, and the maximum contraction possible is only 1/6·75 of the whole volume.

Bunsen's explosion vessel was of glass, and contained a column of gas 1·7 centimetres diameter and 8·15 centimetres long; the electric spark traversed the entire length of the tube so as to secure immediate inflammation of the whole mass of gas.

Clerk has made experiments in a large cast-iron vessel comparable in dimensions to the cylinder of a six-horse-power gas engine. It is a cast-iron cylinder truly bored out and the end covers turned, internal dimensions 7 inches diameter and 8½ inches long, capacity 317 cubic inches. Upon the upper cover is placed a Richards indicator, in which the reciprocating drum has been replaced by a revolving one; the rate of revolution is adjusted by a small fan, a weight and gear giving the power. The cylinder is filled with the explosive mixture to be tested, the drum set in motion, the pencil of the indicator pressed gently against it, and the electric spark passed within the cylinder. The drum is enamelled, and the pencil is a black lead one. The pressure of the explosion acts upon the indicator piston, and a line is traced upon the drum which shows the rise and fall of pressure. The rising line traces the progress of the explosion, the falling line the progress of loss of pressure by cooling. Fig. 1 shows the arrangement of the apparatus. Experiments with hydrogen and air mixtures gave the results shown in the table, p. 395.

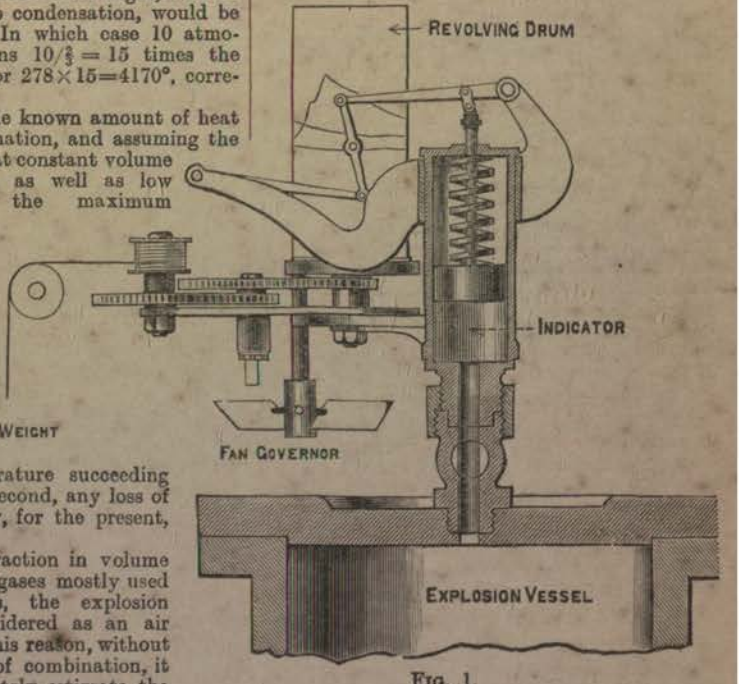


FIG. 1.

The curves of explosion from which these figures are deduced are given at Fig. 2

The rate of cooling is comparatively slow; for instance, in all these experiments, at the end of 0·66 second from the beginning of explosion there still remains above 20 lbs. per sq. inch above atmospheric pressure. The explosion is followed by a very slow fall of pressure.

Several terms have been used somewhat vaguely by engineers dealing with gaseous explosions. It is well to define them accurately.

MIXTURES OF HYDROGEN AND AIR (CLERK).

Experiment	Temp. before explosion 16°. Pressure 14·7 lbs. (atmospheric)				
	Mixture		Max. pressure above atmosphere in lbs. per sq. inch.	Time of explosion	Max. temp. of explosion
	H	Air			
a	1 vol.	6 vols.	41	0·15 sec.	826° to 909°
b	1 vol.	4 vols.	68	0·026 sec.	1358° to 1539°
c	2 vols.	5 vols.	80	0·01 sec.	1615° to 1929°

The rapidity of increase of pressure is the measure of explosiveness, and therefore the time occupied from the commencement of increasing pressure to the moment of maximum pressure is called the *time of explosion*. The explosion is complete when maximum pressure is attained, but it does not follow that the combustion is complete. *Combustion* means burning, not mere ignition, and *complete combustion* means that the burning of carbon to carbonic acid and hydrogen to water has been completed. So long as any portion of combustible remains uncombined with oxygen, the combustion is incomplete.

Complete inflammation is the complete filling of the explosion vessel with flame—that is, the complete ignition of every portion of the explosive mixture, and the gases not entering into the chemical action are ignited as well as those acting. It does not follow that complete inflammation coincides with maximum pressure; it may precede it.

In *Experiment a* (Fig. 2) the mixture is diluted and the flame spreads slowly, the time of explosion being 0·15 second, and when maximum pressure is attained (see Fig. 2), it remains constant for a time, showing that, although explosion is complete, yet combustion is still proceeding at a rate sufficient to compensate for loss of heat to the cold walls.

Experiment b, the time of explosion is 0·026 second, and fall of pressure commences almost immediately that maximum is attained.

In *Experiment c* the explosion is so rapid that the indicator piston cannot register fast enough, and consequently oscillates; the time of explosion is less than 0·01 second.

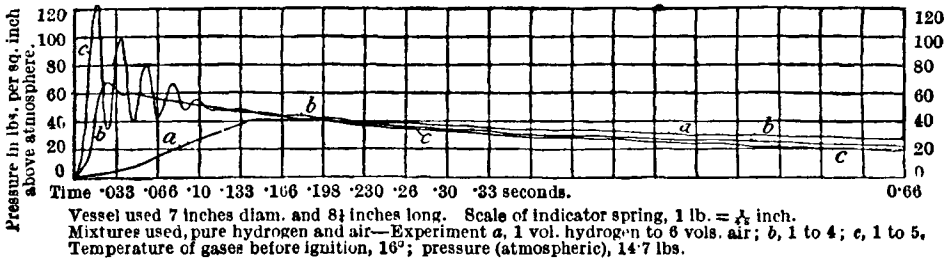
The maximum temperatures are calculated on the two extreme assumptions of complete contraction and no contraction. It will be observed that the range of error becomes less as dilution increases.

Calculating from these curves the total heat accounted for by maximum pressure, and allowing for loss of heat to the walls during time of explosion, as estimated from the falling curves, a great deficiency becomes evident.

Experiment	*a*	*b*	*c*
Heat of combustion of hydrogen present	100	100	100
Heat accounted for by maximum temperature and loss previous to its attainment . .	55	70	54

Even with hydrogen and air mixtures the deficiency ranges from 30 to 46 p.c. It is remarkable that the deficiency at the temperature of about 900° is identical with that at about 1800° within the limits of error. It should be noted, however, that this method of allowing for heat loss will probably give a low value, as no account is taken of the difference in the action of the walls on the rising and falling lines, nor of the possible difference in radiation.

Limits of inflammability.—A mixture of 1 vol. H and 7 vols. air cannot be exploded by



Vessel used 7 inches diam. and 8½ inches long. Scale of indicator spring, 1 lb. = $\frac{1}{15}$ inch.
Mixtures used, pure hydrogen and air—Experiment *a*, 1 vol. hydrogen to 6 vols. air; *b*, 1 to 4; *c*, 1 to 5.
Temperature of gases before ignition, 16°; pressure (atmospheric), 14·7 lbs.

FIG. 2.

the electric spark or by flame at atmospheric pressure and temperature (Clerk).

According to Harold Dixon, 2 vols. H and 1 vol. O, if diluted with 8 vols. of oxygen, ceases to be ignitible, and the same mixture with 7 vols. of nitrogen becomes noninflammable. A mixture which readily ignites in a large vessel cannot be fired in small tubes.

If the pressure of a true explosive mixture, such as electrolytic gas, is reduced sufficiently, it ceases to be ignitible. Electrolytic gas, if reduced to $\frac{1}{8}$ atmosphere, will not fire, but if heated considerably at constant pressure it will do so. Experimenters differ considerably in statements of limits of inflammability: differences in strength of spark, dimensions of vessel, and temperature cause variation, but all agree that reduction of pressure, dilution with excess of any gas, and use of small vessels destroys inflammability, whilst increase of pressure, preliminary heating, and large vessels increase inflammability.

Three vols. of marsh gas added to 2 vols. H and 1 vol. O prevent ignition, whilst 1½ vols. of

ethylene added to the same mixture prevent firing. This fact has an important bearing in practice; a mixture will bear considerable dilution with air, but very little excess of coal gas before losing explosiveness.

Rate of explosion in hydrogen mixtures.—Bunsen first determined the velocity of flame propagation in explosive mixtures. His method is as follows:—

The explosive mixture is allowed to burn from a fine orifice of known diameter in a metal plate, and the current of issuing gas regulated by diminishing the flow until the flame passes back and ignites the mixture. This occurs when the velocity of issue is inappreciably less than the velocity of propagation of flame from layer to layer, from ignited to unignited portion of the mixture. At atmospheric pressure and temperature Bunsen determined the velocity in a mixture of 2 vols. H and 1 vol. O as 34 metres per second. Objections exist against the method. The mixture issuing as flame drags air into it and so cools. The metal plate also exercises a cooling effect, and if the hole were small enough the flame could not pass back at all, as the heat would be conducted away rapidly enough to extinguish the flame, as with the safety lamp. Mallard and Le Chatelier made experiments designed to obviate these objections. The mixture is contained in a long tube of considerable diameter, closed at one end and freely open to the air at the other. At each end a short rubber tube terminates in a cylindrical space closed by a flexible diaphragm. A light style is fixed upon each of the diaphragms. A cylinder revolves close to each style, both cylinders upon the same shaft. A tuning fork, marking the cylinder, determines the rate of revolution. The mixture is first ignited at the open end, and the flame, in passing the lateral opening leading to the first diaphragm, ignites the mixture there, and so moves the style and marks the cylinder; the arrival of the flame at the other end is signalled in the same way.

Determined in this way, Mallard and Le Chatelier estimate the velocity in hydrogen mixture (2 vols. O and 1 vol. H) as 20 metres per second, and in diluted mixtures:

Velocity of explosion in diluted mixtures (Mallard and Le Chatelier):

Mixtures	Metres per second
2 vols. H, 1 vol. O+1 vol. O	=17·3
2 „ H, 1 „ O+3 vols. O	=10·0
2 „ H, 1 „ O+1½ „ H	=18·0
2 „ H, 1 „ O+6 „ H	=11·9
2 „ H, 1 „ O+6 „ H	= 8·1

A large excess of hydrogen causes little diminution in velocity compared with oxygen. With hydrogen and air mixtures the following numbers were obtained:—

Velocity of explosion in hydrogen and air mixtures (Mallard and Le Chatelier):

Mixtures		
2 vols. H and 8 vols. air	=2	metres per second.
2 „ H „ 6 „	=2·8	„
2 „ H „ 4⅔ „	=3·4	„
2 „ H „ 3½ „	=4·1	„
2 „ H „ 3 „	=4·4	„
2 „ H „ 2 „	=3·8	„
2 „ H „ ⅔ „	=2·3	„

Strangely enough, the velocity is greatest when there is considerable excess of hydrogen. A mixture containing 2 vols. H and 5 vols. O has just enough oxygen for complete combustion, but the velocity is greatest when 2 vols. H have only 3 vols. of air.

These numbers are stated to be correct within 10 p.c.; they are all the rates of transmission of flame backwards from the open end of a tube to the closed end, and they are practically the rates of movement at constant pressure, without projection of ignited gases into unignited. When firing from the closed end of the tube very high and variable velocities were obtained: here, not only does the mixture ignite from particle to particle at a rate depending on inflammability alone, but the expansion of the ignited portion causes it to be projected into the unignited, and so increases the rate of ignition. In a closed vessel, the portion first fired expands and compresses the unignited gases into smaller space, and ignition goes on at a continually accelerated rate until complete.

With the same tube fired at the closed end a velocity of 1000 metres per second was obtained with a mixture of 2 vols. H and 1 vol. O, instead of 20 metres per second as fired from the open end.

The velocity of ignition in Clerk's experiments, in a closed vessel, for a mixture of 1 vol. H, 4 vols. air, is equal to about 8 metres per second, 2 vols. H and 5 vols. air, about 20 metres per second.

The explosive wave.—With long tubes, of relatively small diameter, velocities of previously unsuspected magnitude are obtained. Berthelot and Vieille used a straight horizontal leaden tube, 42·45 metres long and 5 millimetres internal diameter, filled it with electrolytic mixture of H and O at atmospheric pressure and temperature, and arranged two metal strips passing across the tube at the ends; a current passed through these strips, and the explosion destroyed them on arriving; the times of interruption of the circuit were recorded by a chronograph, and so the rate of explosion was known. For this mixture, a mean result, from many experiments of 2810 metres per second was found. The velocity was the same in tubes varying from 5 to 35 mm. in diameter, but with a tube of 1·5 mm. the velocity fell to 2341 metres. The maximum velocity is not attained till the explosion has travelled some distance from the point of origin, as shown by the following table:—

DURATION PRECEDING ESTABLISHMENT OF EXPLOSIVE WAVE (BERTHELOT).

Distance of registering points from point of ignition	Mean velocity	
	from origin	in each interval
metres	metres per sec.	metres per sec.
0·02	72·7	72·7
0·05	146·2	448·0
0·50	924·4	2261·0
5·25	2491	3031
20·19	2649	2710
40·43	2679	2706

The velocity rapidly increases up to half a metre; beyond this it is practically constant within experimental error.

The inflaming spark must be a powerful one; if weak, much greater distance is required to establish the explosive wave.

Harold Dixon confirms Berthelot's figures, and as a mean of ten experiments, finds a velocity of 2819 metres per second. Berthelot considers that change of pressure does not affect the explosive rate; but Dixon finds that with electrolytic mixture at 300 mm. mercury, 2670 metres per second is the velocity, and at 1500 mm. mercury 2917 metres per second.

The velocity does not increase indefinitely with increase of pressure, but at 1100 mm. mercury practically attains a maximum.

The rate of the explosive wave diminishes with dilution with an excess of any gas; mixture 2 vols. H, 1 vol. O+8 vols. O, rate of explosion 1075 metres per second (Harold Dixon); 2 vols. H, 1 vol. O+5 vols. O=1650 metres per second; 2 vols. H, 1 vol. O+5 vols. N=1782 metres per second—all for atmospheric pressure and temperature. It appears that although ignition is arrested by less excess of nitrogen than oxygen, yet nitrogen retards the rate of explosion less than oxygen.

Explosion of mixtures of carbonic oxide and oxygen.—The maximum pressure produced by explosion of 2 vols. CO and 1 vol. O at atmospheric pressure and temperature 4·5° is 10·8 atmospheres (Bunsen), corresponding to a temperature of 2612° assuming no contraction, and 4140° assuming complete contraction due to combination. The maximum temperature calculated from heat of combustion at constant volume is 12,820°, so that here also a great difference exists between heat evolved and heat accounted for. Dilution with excess of any gas reduces the pressure attained and lengthens the time of explosion, as with hydrogen.

Berthelot found time of explosion in a closed vessel 300 c.c. capacity, of this mixture (2 vols. CO+1 vol. O) to be 0·0128 second; and in a vessel of 4000 c.c. capacity, 0·0155 second.

By Bunsen's method, the velocity of inflammation at constant pressure is 1 metre per second nearly, and by Mallard and Le Chatelier's method, also at constant pressure, it is 2·2 metres per second.

The velocity of the 'explosive wave' (Berthelot) is 1090 metres per second, excited under similar circumstances to the hydrogen experiments. Harold Dixon has observed the remarkable fact that a mixture of carbonic oxide and oxygen, if thoroughly dried over phosphoric anhydride, could not be fired by the electric spark, but that, a trace of moisture added, the spark at once takes effect. He has made determinations of the rate of the explosive wave on mixtures 2 vols. CO and 1 vol. O, in which different quantities of water vapour are present, and finds that a well-dried but not absolutely dry mixture gave a velocity of 1264 metres per second, while, when saturated with steam at 35°, the rate rose to 1738 metres per second. The explosion travelled 10 feet before arriving at the first registering point, so that velocity might be a maximum before commencing measurements. This seems to indicate that water vapour enters into the reaction of the oxidation of CO, even when the explosive wave is propagated.

Explosion of mixtures of coal gas and air.—Experiments have been made by Clerk with mixtures of coal gas and air in the explosion apparatus already described, with the following results:—

GLASGOW COAL GAS AND AIR MIXTURES (CLERK).

Temperature of gases before ignition, 18°. Pressure of atmosphere (14·7 lbs.)				
Experiment	Proportion of gas by volume	Maximum pressure in lbs. per sq. inch above atmosphere	Maximum temperature centigrade	Time of explosion
a	$\frac{1}{14}$	52	1047°	0·28 second
b	$\frac{1}{12}$	63	1266°	0·18 ,,
c	$\frac{1}{10}$	69	1384°	0·13 ,,
d	$\frac{1}{9}$	89	1780°	0·07 ,,
e	$\frac{1}{8}$	96	1918°	0·05 ,,

From these experiments, it will be observed that the greatest possible pressure exerted by a mixture of Glasgow coal gas and air at atmospheric pressure and temperature is 96 lbs. per square inch above atmosphere, the maximum pressure falls as dilution with air increases, while the time of explosion also increases. The shortest time of explosion is $\frac{1}{20}$ second, and the longest over $\frac{1}{4}$ second, at the end of 0·60 second from 30 to 35 lbs. per square inch pressure above atmosphere still remains in the vessel. It is very noticeable that, volume for volume, coal gas produces higher pressure than hydrogen.

Experiments with Oldham gas and air give the results shown on p. 398.

The greatest pressure produced by a mixture of this gas and air is 91 lbs. per square inch above atmosphere. Comparing these numbers with the Glasgow gas experiments, it appears that with $\frac{1}{12}$ vol. of Oldham gas present, the pressure attained is 0·5 lb. per square inch less, and the time of explosion is 0·31 second against 0·28 second with the same proportion of Glasgow gas. With $\frac{1}{8}$ of the two gases, Oldham is 5 lbs. less maximum pressure and 0·055 second against 0·05 second Glasgow. At Fig. 3 are shown reduced copies of the lines of explosion and cooling from which these values have been deduced.

In all these experiments the suppresssion of heat at the maximum temperature is very considerable, ranging from 50 to 60 p.c.

Experiments have been made by Clerk in

OLDHAM COAL GAS AND AIR MIXTURES (CLERK).

Experiment	Proportion of gas by volume	Maximum pressure in lbs. per sq. inch above atmosphere	Maximum temperature centigrade	Time of explosion
	Temperature of gases before ignition, 17°. Pressure of atmosphere (14·7 lbs.)			
a	1/15	40·0	806°	0·45 second
b	1/14	51·5	1033°	0·31 ,,
c	1/13	60·0	1202°	0·24 ,,
d	1/12	61·0	1220°	0·17 ,,
e	1/10	78·0	1557°	0·08 ,,
f	1/8	87·0	1733°	0·06 ,,
g	1/7	90·0	1792°	0·04 ,,
h	1/6	91·0	1812°	0·055 ,,
i	1/5	80·0	1595°	0·16 ,,

the same vessel with mixtures previously compressed, and it is found that the pressures produced with any given mixture are proportional to the pressure before ignition—that is, with a mixture of constant composition, double the pressure before explosion, keeping the temperature constant, doubles the pressure of explosion. A mixture of 1 vol. coal gas and 15 vols. air cannot be fired by the electric spark (Clerk), and 1 vol. gas 3 vols. air contains too great an excess of gas to fire. It is somewhat remarkable that a slight excess of coal gas causes more rapid ignition, and further increase acts more rapidly in checking rates of ignition than air.

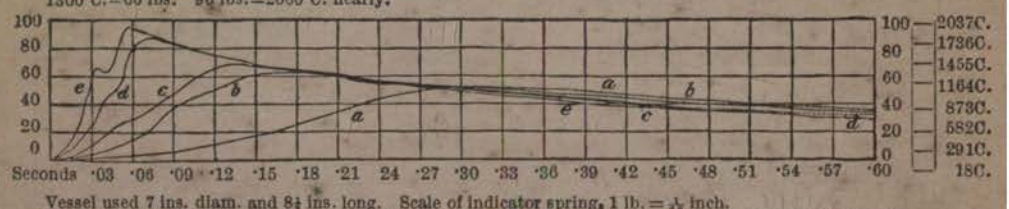
Experiment and practice agree that the best mixture for use in gas engines lies between 1 vol. gas to from 9 to 11 vols. other gases.

Rate of explosion in coal gas and air mixtures.—Mallard and Le Chatelier have determined the rate of explosion at constant pressure in their apparatus of mixtures of coal gas and air.

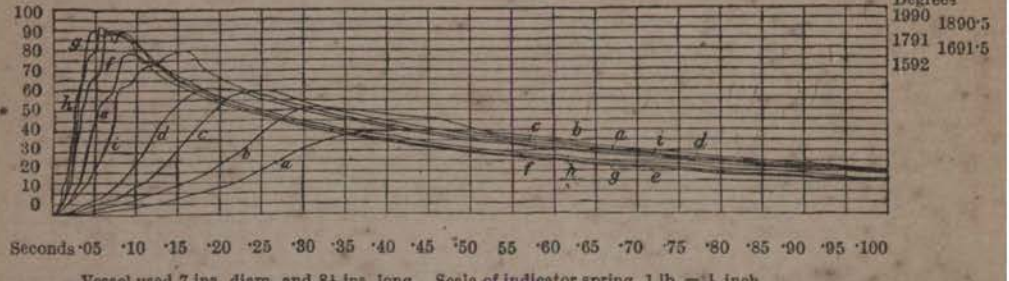
Velocity of explosion in coal gas and air mixtures (Mallard and Le Chatelier):

Mixture	Velocity
1 vol. gas, 7 vols. air	. 0·83 metres per second
,, 5·6 ,,	. 1·00 ,,
,, 4·7 ,,	. 1·16 ,,
,, 4·0 ,,	. 0·90 ,,

The maximum velocity is here also attained with a slight excess of coal gas. The 'explosive wave' can also be generated in coal gas and air mixtures, but little attention has been paid as yet to its rate of propagation. Clerk's experiments in a closed vessel give the maximum velocity of inflammation of gas and air mixtures as about 5 metres per second, with ¼ vol. of coal gas present (Oldham experiments).



Vessel used 7 ins. diam. and 8½ ins. long. Scale of indicator spring, 1 lb. = 1/10 inch.
Mixtures used Glasgow coal gas and air. Experiment *a*, 1 vol. gas to 13 vols. air; *b*, 1 to 11; *c*, 1 to 9; *d*, 1 to 7; *e*, 1 to 5.
Temperature of gas before ignition 18°, pressure atmospheric.



Vessel used 7 ins. diam. and 8½ ins. long. Scale of indicator spring, 1 lb. = 1/10 inch.
Mixtures used, Oldham coal gas and air. Experiment *a*, 1 vol. gas to 14 vols. air, temp. (of explosion and measuring vessels) 18°; *b*, 1 to 13, 16·2°; *c*, 1 to 12, 16°; *d*, 1 to 11, 16·1°; *e*, 1 to 9, 16·7°; *f*, 1 to 7, 16·7°; *g*, 1 to 6, 16°; *h*, 1 to 5, 16°; *i*, 1 to 4, 19°.
Centigrade temperatures, assuming no loss of volume, owing to combination of mixtures. Atmospheric pressure, 14·7 lbs., and mean temperature before ignition, 17°.

FIG. 3.

In 1900 Clerk made further experiments with London coal gas and air, with very complete precautions to ensure mixing, and with more accurate timing devices. The curves obtained with this apparatus are shown at Fig. 4, and the maximum temperatures and pressures, and time of explosion for the different mixtures, are as follows :—

EXPLOSION IN A CLOSED VESSEL (CLERK, 1900).

Mixtures of air with London coal gas.

Temperature before explosion 16°
Pressure before explosion . 14·8 lbs. per sq. in.

Mixture		Max. pressure above atmosphere in lbs. per sq. inch	Temp. of explosion from observed pressure	Time of explosion
Gas	Air		°C.	sec.
1 vol.	12 vols.	4	—	—
1 „	11 „	58	1150	0·290
1 „	10 „	60	1155	0·305
1 „	9 „	65	1270	0·155
1 „	8 „	77	1475	0·087
1 „	7 „	80	1565	0·067
1 „	6 „	85	1660	0·055
1 „	5 „	87	1710	0·042
1 „	4 „	93	1830	0·045

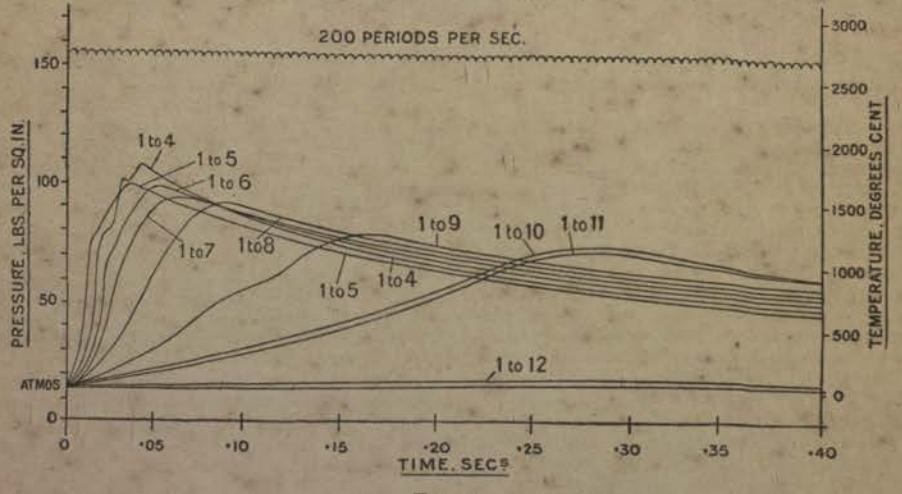


FIG. 4.

Explosion in a closed vessel, London gas, 1900 (Clerk).

These experiments have been repeated with different indicating devices at the Massachusetts Institute of Technology, and the method has been applied to mixtures of air and petrol vapour. The results for air and petrol vapour are given below:

EXPLOSION IN A CLOSED VESSEL. (BOSTON EXPERIMENTS.)

Mixtures of air and petrol vapour.

Petrol, sp.gr. 0·648 at 86°F.

Percentage of petrol vapour mixture	Time of explosion: seconds	Max. press. in lbs per sq. in. above atmosphere	0·2 sec. after maximum pressure			
			Area, sq. inch	Mean pressure lbs. per sq. in.	Mean pressure ÷ vapour ratio	Final pressure
1·51	0·083	70	1·48	49·4	3260	34
1·64	0·100	73	1·53	51·0	3110	36
1·79	0·090	71	1·43	47·7	2670	33
1·96	0·083	76	1·35	51·7	2634	35
2·17	0·058	70	1·45	48·4	2225	30
2·44	0·067	80	1·60	53·4	2190	36
2·56	0·075	84	1·69	56·4	2200	40
2·63	0·059	86	1·71	57·0	2164	38
2·78	0·083	78	1·62	54·0	1945	36
3·03	0·091	76	1·60	53·4	1760	38
3·23	0·083	77	1·62	54·0	1675	37
3·45	0·083	77	1·64	54·7	1587	37
3·85	0·075	66	1·50	50·0	1300	38
4·17	0·066	60	1·38	46·0	1104	35
4·76	0·066	56	1·32	44·0	925	33

Petrol, sp.gr. 0·680 at 76°F.

Percentage of petrol vapour in mixture	Time of explosion : seconds	Max. press. in lbs. per sq in. above atmosphere	0·2 sec. after maximum pressure			
			Area sq. inch	Mean pressure lbs. per sq. in.	Mean pressure ÷ vapour ratio	Final pressure
1·32	0·167	52	1·28	42·7	3240	33
1·41	0·117	62	1·42	47·3	3360	35
1·51	0·109	64	1·45	48·6	2950	35
1·64	0·182	51	1·25	41·7	2540	32
1·79	0·109	67	1·53	51·0	2855	36
1·96	0·091	73	1·53	51·0	2600	36
2·17	0·082	76	1·56	52·0	2391	37
2·44	0·060	85	1·63	54·3	2225	36
2·63	0·058	85	1·62	54·0	2052	36
2·78	0·058	84	1·64	54·7	1970	38
3·03	0·066	78	1·60	53·4	1760	37
3·23	0·067	83	1·70	56·7	1760	38
3·45	0·100	75	1·59	53·0	1536	38
3·85	0·117	62	1·42	47·3	1230	35
4·17	0·133	55	1·40	46·7	1121	38
4·76	0·210	35	1·02	34·0	714	32

Column 4 of this table requires some explanation. The area in square inches signifies the area under the cooling curve from maximum pressure to one-fifth of a second after, and the mean pressure in column 5 is taken from this area, as determined by planimeter. The experiments show clearly that the best mixture of petrol and air with petrol of 0·648 sp.gr. is 1·51 p.c. of petrol vapour in the air mixture, and with petrol of 0·680 sp.gr., 1·41 p.c.

In 1895 Mr. F. Grover, of the University of Leeds, made similar experiments, and, among other mixtures, dealt with the explosion of mixtures of acetylene and air.

Fig. 5 shows the explosion diagrams for various mixtures igniting at atmospheric pressure; and Fig. 6 shows diagrams ignited at 2 atmospheres initial pressure. The maximum pressures obtained and time of explosion are given below:

MIXTURES OF ACETYLENE AND AIR EXPLODED AT ATMOSPHERIC PRESSURE (GROVER).

Initial temperature, 0°.

Proportion of air to gas	air	18	15	14	13	12	11	10	9	8	7	6	5	4
	gas	1	1	1	1	1	1	1	1	1	1	1	1	1
Maximum pressure in lbs. per sq. inch above atmosphere		54	74	83	83	89	95	103	108	111	112	106	102	101
Time of explosion in seconds			0·085		0·061		0·047			0·034				

MIXTURES OF ACETYLENE AND AIR EXPLODED AT TWO ATMOSPHERES PRESSURE (GROVER).

Initial temperature, 0°.

Proportion of air to gas	air	21	20	19	18	17	16	15	14	13	12	11	10	9	8
	gas	1	1	1	1	1	1	1	1	1	1	1	1	1	1
Maximum pressure in lbs. per sq. inch above atmosphere		121	127	115	138	129	143	171	159	170	168	177	166	196	179
Time of explosion in seconds		0·10		0·10		0·08				0·035		0·06		0·025	

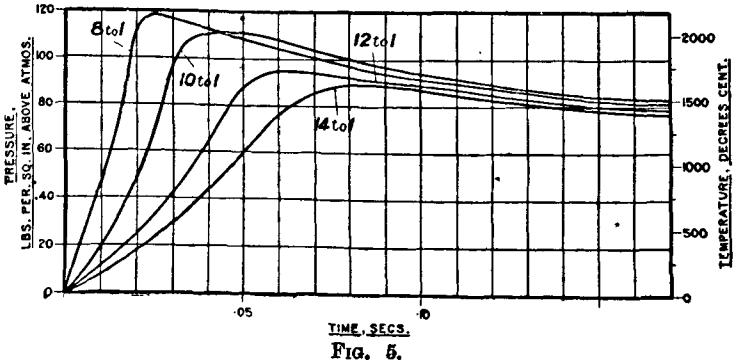


FIG. 5.

Various mixtures of acetylene and air ignited at atmospheric pressure (Grover).

Petavel has also made experiments on the explosion of coal gas and air compressed before ignition to pressures of over 1000 lbs. per square inch. Fig. 7 (p. 402) shows the diagrams obtained, with the particulars marked thereunder.

Experiments have also been made by Bairstow and Alexander, at the Royal College of Science. In these experiments, coal gas and air were ignited at initial pressures of from 7 to 45 lbs.

In all these experiments, it is clear that if the temperature be calculated from the maximum pressure of explosion, there is apparently a suppression of heat of a very considerable amount at maximum temperature, the amount being about 60 p.c.; and Bairstow and Alexander calculate, allowing for heat loss, that the heating value of the gas, measured by the rise of temperature corrected for cooling, is only 65·7 p.c. of the calculated value, for a mixture containing 1 vol. of gas to 5·3 vols. of air; while for a mixture containing 1 vol. of gas to 9·8 vols. of air, the rise of pressure is 80 p.c. of the calculated value.

Important experiments have also been made by Prof. Hopkinson, of Cambridge University. Prof. Hopkinson investigated the actual temperatures reached during explosions of coal gas

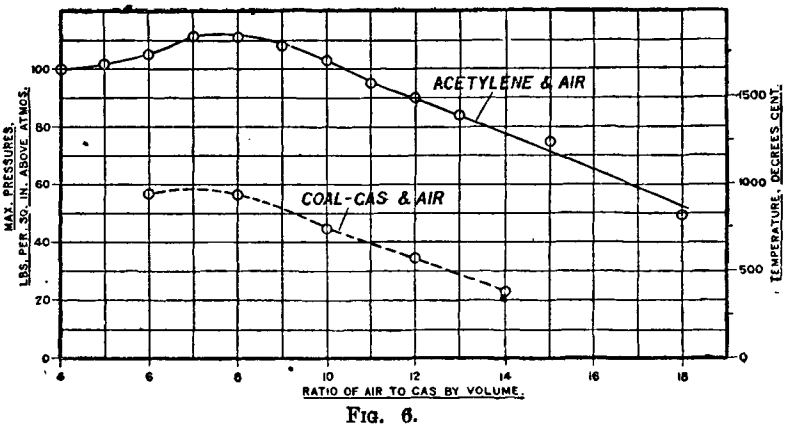


FIG. 6.

Maximum pressure recorded when exploding mixtures of acetylene and air, also coal gas and air. Initial pressure, 1 atmosphere; Initial temperature, 0°C. (Grover).

and air in an explosion vessel of the form shown at Fig. 8, and found very large temperature variations at different parts of the vessel, and that the temperature differences existed after complete inflammation, quite independently of the local cooling effect of the walls of the vessel. He found that after the explosion of coal gas and air in the vessel, the distribution of temperature at the moment of maximum pressure was roughly as follows:—

Mean temperature (inferred from pressure)	1600°
Temperature at centre of vessel, thermometer B	1900°
Temperature 10 cm. (4 inch) within wall, thermometer C	1700°
Temperature 1 cm. (0·4 inch) from wall, at end, thermometer D	1100° to 1300°
Temperature 1 cm. (0·4 inch) within wall at side	850°

Half a second after maximum pressure, the distribution was as follows:—

Mean temperature (inferred from pressure)	1100°
Mean temperature, exclusive of layer 1 cm. thick at walls, determined by long platinum wire from B to D	1160°
Temperature at centre of vessel, thermometer B	1100° to 1200°

Here the temperature differences are much smaller than at the moment of maximum pressure. Hopkinson found that the explosion vessel is entirely filled with flame when the pressure reaches 70 lbs., although the maximum pressure attained later is 82 lbs. per square inch above atmosphere; that is, maximum pressure is not attained until one-thirtieth of a second after the vessel is completely filled by flame. Hopkinson's experiments also distinctly prove that the highest temperature reached in the vessel is at the point of origin of the ignition, and is due to the compression of the gases which are first heated by explosion to about 1200°, and then compressed by the compression from the walls inwards, as the mixture near the walls inflames.

Explosion in gas-engine cylinders.—In all internal-combustion engines in general use at the present time, the mixture of fuel and air is compressed before ignition, the maximum temperature ranging from 1200° to 2500°; while the temperature of the hot gases at the moment of opening the exhaust valve may be about 1000°. Fig. 9 is a reproduction of an indicator diagram of an internal-combustion engine working on the Otto cycle. The effect of weakening the mixture is shown by the different lines on the diagram. The line *a* shows a diagram obtained from a strong mixture; *b*, a diagram from a slightly weaker mixture; and *c*, a diagram obtained from a very weak mixture. The effect of apparent suppression of heat appears on the gas-engine diagram as well as in the diagrams obtained by explosion in closed vessels at constant volume, referred to above; and it is extremely important, for the purpose of a correct theory of the internal-combustion

engine, to ascertain exactly what takes place on explosion, and immediately after explosion of the mixture used; and a complete knowledge of the thermal properties of the working fluid and its chemical composition at any instant during the cycle is necessary.

In the normal gas-engine diagram, the expansion line is at first usually considerably above the adiabatic, showing that the whole of the heat of combustion is not added before maximum pressure, and that heat must be added to the gases during a portion of the expansion, to make up for the flow of heat through the cylinder walls. If, however, the cooling on expansion is too great, the expansion line may fall below the adiabatic, although there is still heat being added. The adiabatic expansion line for any given mixture of gases depends on the specific heat of the mixture, and therefore, in order to determine what are the conditions as regards addition of heat, it is necessary to know the specific heat or internal energy of the mixture at any given temperature.

Clerk has investigated the properties of the working fluid in the gas engine itself, by a method which allowed direct observation to be made upon an actual charge taken into the engine in the ordinary operations of its cycle. The method consists in subjecting the whole of the heated products of combustion to alternate compression and expansion, within the engine cylinder, while the cooling proceeds, and observing by the indicator the successive pressure falls from revolution to revolution, together with the temperature and pressure rise and fall due to the alternate compression and expansion.

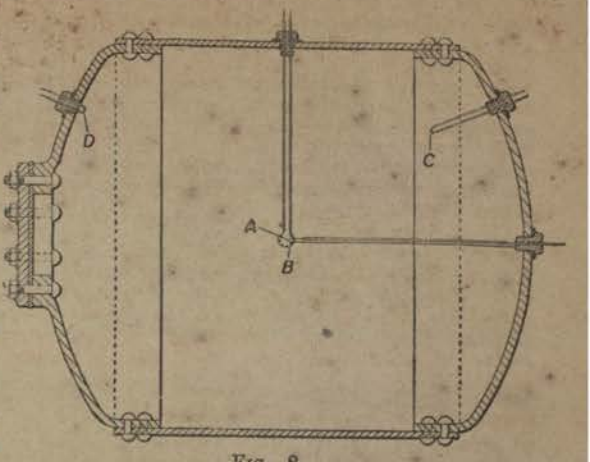


FIG. 8.

Hopkinson's Explosion Vessel.

The engine is set to run at a given speed, and after the charge of gas and air has been drawn

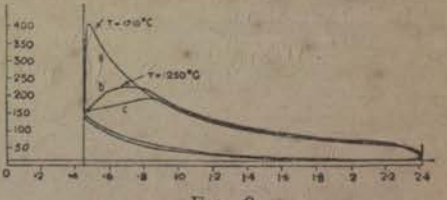
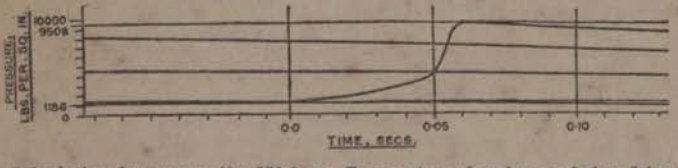


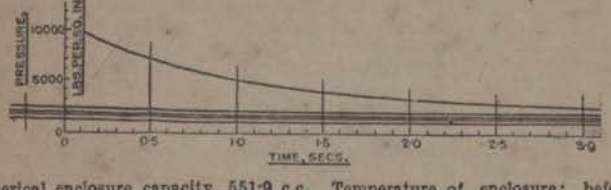
FIG. 9.

in, compressed and ignited, the exhaust valve and inlet valve are prevented from opening, so that when the piston reaches the end of its power stroke, the exhaust gases are retained within the cylinder, and compressed by the piston to the maximum volume, and again allowed to expand and again compressed, and so on. These operations give a diagram as shown at Fig. 10. From this diagram, by determining the temperature fall due to work done on expansion, Clerk determined the apparent specific heat of the products of combustion, and found that for the gas-engine mixture there was a considerable rise of apparent specific heat with temperature, and it seemed probable that this was largely due to a real increase of the actual specific heat or internal energy of the gases at high temperatures. The experiments, however, could not differentiate



Spherical enclosure capacity, 551·9 c.c. Temperature of enclosure: before firing, 18°C.; after firing, 24°C. Initial pressure, 1136 lbs. per sq. inch. Maximum pressure, 9508 lbs. per sq. inch. Ratio $\frac{\text{Air}}{\text{Gas}} = 6{\cdot}0$.

$$\text{Ratio } \frac{\text{Maximum pressure}}{\text{Initial pressure}} = 8{\cdot}36.$$



Spherical enclosure capacity, 551·9 c.c. Temperature of enclosure: before firing, 21°C.; after firing, 27°C. Initial pressure, 1094 lbs. per sq. inch. Maximum pressure, 9618 lbs. per sq. inch. Ratio $\frac{\text{Air}}{\text{Gas}} = 5{\cdot}71$.

$$\text{Ratio } \frac{\text{Maximum pressure}}{\text{Initial pressure}} = 8{\cdot}8.$$

FIG. 7.

Rise and Fall of Pressure during and after Explosion (Petavel).

between the effects produced by dissociation and real specific heat change. Further, the values obtained were subject to some uncertainty, due to the difficulty of apportioning heat loss between successive compression and expansion lines, and it is probable that the values are somewhat raised by some film phenomena, or by smouldering combustion, tending to keep the expansion line from falling as rapidly as it would otherwise do.

Work of the British Association Committee on Gaseous Explosions.—Owing to the great importance to the theory of the internal-combustion engine of a complete understanding of the phenomena of gaseous explosions, the British Association appointed a committee for the purpose of investigating the whole matter, and although the work of this committee is not yet completed, very important results have already been obtained. These are set out in the Reports of 1908, Dublin; 1909, Winnipeg; and 1910, Sheffield. The committee regard it as proved that on the explosion of gaseous mixtures with air, the quantity of carbonic acid or steam dissociated at the temperature of the explosion is so small, that the suppression of heat cannot be due to this cause.

They also conclude that chemical equilibrium is complete within an extremely short period after inflammation at any point outside the influence of the walls, and that there is no time rate of combustion, such as will account for the apparent suppression of heat.

The committee have also made a very careful comparison of the specific heat found by Holborn and Henning by methods not depending on explosion, with the values found by explosion experiments, such as those of Clerk, Mallard, and Le Chatelier, and Langen. The results given in calories per gram-molecule for the internal energy calculated from 100° at temperatures of 800°, 1200°, 1600°, and 2000°, are as follows:—

	800°		1200°		1600°	2000°
	Clerk	Holborn and Henning	Clerk	Holborn and Henning	Langen	Langen
Air	—	3570	—	5840	8700	11500
CO_2	—	6460	—	10880	17000	23300
H_2O	—	4670	—	7930	14400	19900
Gas-engine mixture	4250	3840	6900	6340	9800	13200
Ideal gas*	3430		5400		7350	9300

* $C_v = 4{\cdot}9$.

In this table, in order to reduce to foot-lbs., the figures should be multiplied by the factor 3·96. The agreement between the figures by the two methods shows that the suppression of heat is very largely due to increase in the real specific heat at high temperatures.

It seems clear also that the cooling due to the walls of the explosion vessel will damp out a certain portion of the combustion, and thus give a certain time rate of combustion, so that all the heat is not actually evolved at the point of maximum pressure or maximum temperature. By arranging a moving piston so that the exhaust products can be collected, and immediately cooled at any instant during the expansion stroke, Clerk has shown from an analysis of the exhaust products that there is still some uncombined gas after the point of maximum temperature has been reached, even with strong mixtures.

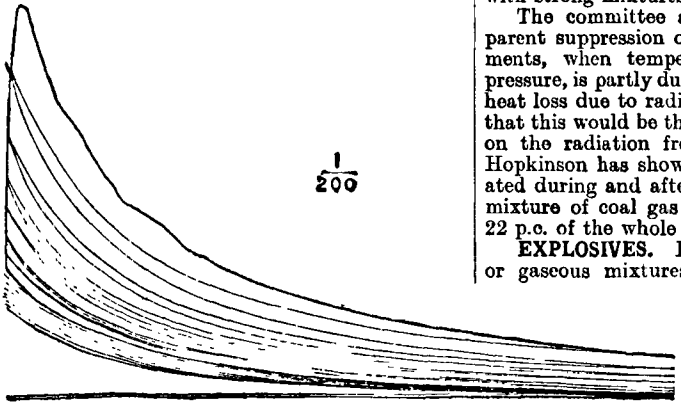


FIG. 10.

Clerk diagram from engine at a brake load of 50 H.P. at 160 revolutions per minute.

The committee also consider that the apparent suppression of heat in explosion experiments, when temperature is calculated from pressure, is partly due to under-estimation of the heat loss due to radiation. Callendar predicted that this would be the case from his experiments on the radiation from a Bunsen flame; and Hopkinson has shown that the total heat radiated during and after an explosion of a 15 p.c. mixture of coal gas and air amounted to over 22 p.c. of the whole heat of combustion. D. C.

EXPLOSIVES. Explosives are solid, liquid, or gaseous mixtures or chemical compounds, which by chemical action (set up in them by flame, by a blow, or by other means) generate suddenly large volumes of heated gas.

The rate at which the expansive force, which characterises an explosive reaction, is developed, varies considerably, and determines whether the reaction is a combustion, explosion, or detonation. These terms are purely relative, and there

is no definite line of demarcation between them.

The factors determining the rapidity of an explosive reaction are the chemical nature of the explosive, its physical condition, the conditions under which it is exploded, and the method of firing.

The energetic action of an explosive largely depends on its rate of chemical change; in chemical compounds (like nitroglycerin and guncotton) the reacting atoms are in much greater proximity than are those of a mechanical mixture of solids (such as gunpowder), and in the former class the rapidity of the chemical action will be greater than in those of the latter class, composed of constituents by themselves non-explosive.

The explosives in actual use are instances of oxidation, oxygen being supplied by a nitrate, by nitric acid, by a NO_2 group, or by a chlorate.

The oxidising compounds used in explosive mixtures and explosive compounds are frequently endothermic substances, the heat of decomposition contributing towards the expansion of the gaseous products of the explosion. The conditions for complete combustion of the combustible elements do not always give the maximum explosive effect; carbon burning to monoxide gives a larger evolution of gas, but less evolution of heat than on complete combustion, and the best composition for any given explosive effect has to be determined by experiment.

The physical condition of an explosive has a marked effect on its explosibility and the character of the explosion; frozen nitroglycerin is much less sensitive than the same explosive in the liquid state, and the same gunpowder mixture gives various effects according to the size of the grain.

Confinement increases the effect of all explosives; the more rapid the explosive the less the confinement necessary to obtain its maximum effect. The power of mercury fulminate is but little increased by confinement, but explosives of the gunpowder type require to be strongly confined to produce disruptive effects.

An explosive reaction may be initiated by a heated solid, a flame, by friction, by percussion, an electric spark or current, or by the concussion from another explosion. The nature of the reaction is largely conditioned by the method of firing adopted: nitroglycerin or guncotton in contact with a flame burns quite quietly in the open, but when fired by the detonation of a small initial charge of mercury fulminate, the whole mass of the explosive decomposes practically instantaneously, and detonation results.

Explosives may be classified either according to their chemical composition, into explosive mixtures or explosive compounds; according to their effect and the purpose for which they are employed, into 'high' or 'low' explosives or 'disruptives' and 'propellants'; or according to the danger in handling, transporting, and storing them.

In this article, the chemical classification is adopted, as far as possible. All the substances having explosive properties are not included, but only those that have, or may have, value for practical purposes.

Explosive Mixtures.

In explosive mixtures, the combustible and supporter of combustion are present in separate ingredients, which are usually not in themselves explosive. The necessary speed of reaction is ensured by extremely fine subdivision and very thorough incorporation of the ingredients, and by the oxygen being in a highly concentrated and more or less easily liberated form. An important characteristic of this class of explosives is that their effect may be varied by varying the proportions of the ingredients.

Explosive mixtures may be grouped, according to the source of their oxygen, into nitrate, chlorate, perchlorate, &c., mixtures. Only the mixtures of these oxidising substances with combustible ingredients, in themselves non-explosive, and those containing only a small proportion of an explosive compound added to improve the explosive properties of the mixture, will be considered under this heading. The mixtures of oxidising substances with explosive compounds, where the former are only of secondary importance, will be considered under the respective explosive compounds.

Nitrate Mixtures.

In the nitrates, the oxygen is in sufficiently strong combination to need a somewhat powerful disturbing agency to liberate it, so that the nitrate mixtures are not very sensitive and their action is comparatively slow.

Potassium nitrate mixtures.—Of the various nitrates used in explosive mixtures, the potassium salt is by far the best adapted for the purpose, and black powder, or gunpowder, is the most important member of this class of explosives.

Gunpowder.

Since the introduction of smokeless powders, gunpowder has been gradually superseded for most military purposes: both as a propellant and a disruptive it is obsolescent. It is still, however, very largely used in industrial mining operations, as a propellant for sporting purposes, and, the smaller sizes, for subsidiary military purposes, such as for primers and igniters for large smokeless-powder charges, for fuses, and as an ingredient in certain compositions.

Ordinary black gunpowder consists of an intimate mixture of potassium nitrate, sulphur, and charcoal. The composition of the black powder used for military purposes in different countries is given in the table, p. 405.

English black gunpowders contain about 1 to 1·3 p.c. moisture.

Manufacture.—A short account only of the process of manufacture will be given, mainly that used at the Royal Gunpowder Factory, Waltham Abbey.

The Ingredients.

The *nitre* employed at Waltham Abbey is wholly Indian nitre. As imported, it has been partially purified, but contains potassium and sodium chlorides, potassium, sodium, and calcium sulphates, sand, and organic matter; the total impurities averaging about 4½ p.c. It is submitted to a simple refining process, being first dissolved by heat in the water used for washing the purified nitre of a previous operation. The liquid is heated to boiling in large

refining coppers, the scum on the surface being carefully skimmed off; the temperature of the liquid is allowed to fall to 104°, and it is then filtered through bags of coarse cloth into the crystallising vessels. The temperature of the solution on entering the crystallising vessels is about 88° to 82°, the liquid is kept in constant agitation with wooden hoes, whereby, as the liquid cools, fine crystals are formed. The solution is not stirred when its temperature is lower than 32°. If the solution were left to crystallise undisturbed, large crystals would form, and would enclose mother liquor. The crystals are drawn to the side of the crystalliser, and transferred to draining frames. The drained nitre flour then receives three washings with distilled water in quantities insufficient to dissolve the nitre, each washing is succeeded by draining; after the last washing the nitre is drained all night, and is removed (except the bottom part,

Composition of Black Powder used for Military Purposes.

—	Per 100 dry gunpowder		
	Potassium nitrate	Sulphur	Charcoal
England, Russia, Sweden, Italy, Turkey, United States	75·0	10·0	15·0
France, Belgium, Spain, Persia	75·0	12·5	12·5
Germany	74·0	10·0	16·0
Austria-Hungary	75·5	10·0	14·5
Portugal	75·7	10·7	13·6
Switzerland	76·0	10·0	14·0
Holland	70·0	14·0	16·0
China	61·5	15·5	23·0

which is very moist) to the store bins. After about three days in store it is ready for the powder manufacture, and contains from 3 to 5 p.c. of moisture, according to the season; the water is estimated and allowed for in weighing the charges.

The waters used for washing the crystals are employed for the solution of the crude nitre; the nitre is recovered from the crystallisation mother liquors by evaporation, and is treated as crude nitre.

From Désortiaux, it appears that the agitation of the solution of nitre during crystallisation in order to obtain fine crystals is in general use on the Continent; at least, he mentions it as in use at Lille, Wetteren, and Spandau. At the refineries at Lille, Wetteren, and Spandau, he states that glue is added to the boiling solution of the crude nitre (the weight of glue being about $\frac{1}{3000}$ that of the crude nitre); the glue coagulating and carrying down organic colouring matters. The process of purification was the invention of Béaume and Lavoisier, and existing processes follow theirs with slight modifications.

On the Continent, and by most private manufacturers in this country, artificial saltpetre, or 'German saltpetre,' as it is frequently called, is almost exclusively used. It is made by dissolving 10 parts of sodium nitrate, 'Chile saltpetre,' and 9 parts of potassium chloride, obtained from Stassfurth 'carnallite,' in mother liquors from previous operations, concentrating and crystallisation. It is refined as above.

In 1894 Hellick discovered that 'German saltpetre' frequently contained notable quantities of perchlorate, and it was stated that several accidents in powder factories coincided with the presence of a considerable percentage of perchlorate in the powder. It was subsequently shown that powder containing perchlorate was not unduly sensitive. The perchlorate is, however, not uniformly distributed in nitre, but tends to agglomerate, and the irregular shooting obtained with some foreign sporting powders, as compared with English ones, has been attributed to the contained perchlorate.

The *sulphur* employed at Waltham Abbey is native Sicilian sulphur, of the best quality. In Sicily, the sulphur mineral is subjected to a liquation process, to separate the sulphur from the gangue. It still contains 3 to 4 p.c. gangue, from which it is freed by distillation. It is distilled from a large iron retort, provided with two tubes placed at right angles to each other; one tube (15 inches wide) communicates with a large dome-shaped subliming chamber, the other tube (5 inches wide) enters an iron pot which receives the distilled sulphur; this tube is jacketed for cooling with water. The tubes can be connected with the distilling vessel or cut off from it by means of valves. The distilling vessel receives its charge of sulphur, which is heated to boiling; during the earlier stages of the distillation the vapours are sent into the subliming chamber, where the sulphur condenses as 'flowers of sulphur'; later on the sulphur vapour is sent through the condenser, from which it runs into the receiver in the liquid form. It is allowed to cool somewhat, but not to its solidifying-point, and is ladled into moist wooden moulds. Sulphur, of sufficient purity to be used in explosives without further treatment, is now obtained in large quantities, by the 'Chance-Claus' process, from the calcium sulphide, which is the chief constituent of the residue formed in the manufacture of soda. Much of the sulphur used by private firms and abroad is also obtained from pyrites. The 'flowers of sulphur' are not used in the manufacture of the gunpowder, as they usually contain considerable quantities of sulphurous and sulphuric acids, but are redistilled.

The sulphur igniting in air at a low temperature—about 250°—renders the gunpowder inflammable, and, experience has shown, improves the keeping qualities of the powder.

The *charcoal*. For making the charcoal for gunpowder, soft and light woods are chosen, of an average growth of from two to ten years. The wood should be cut in the spring, when it is in full vegetation, as then its bark can readily be removed; in the spring the tree is in fullest sap, but the sap is very watery, and contains but little salts in solution.

At Waltham Abbey, the woods used are: the alder buckthorn (*Rhamnus frangula*, L., improperly called dogwood), alder, and willow (*Salix alba*, L.). The woods are grown in England, and are cut about four inches in diameter.

Désortiaux states that in France the so-called dogwood (*Rhamnus frangula*) is exclusively employed for making the charcoal for military and sporting powders; he states, however, that it is becoming increasingly difficult to procure, and that they are trying to replace it by willow, or by the wood of the spindle tree. In Germany, 'dogwood' (*R. frangula*), willow, and alder are used; in Russia, alder.

At Waltham Abbey, wood is usually kept for about three years, dogwood in thatched stacks, and willow and alder piled by cords in the open. By the method of carbonisation, there followed, 25 p.c. of black charcoal should be obtained from the wood, rather more from dogwood. The wood is cut into three-feet lengths, which are split if differing much in thickness, and is packed into iron cylindrical cases called slips, 3 feet 6 inches long, and 2 feet 4 inches in diameter. The lid is fastened on, two openings (each about 4 inches in diameter) being left in the bottom of the slip. The slips are then placed in horizontal cylinders, the end of the slip with the openings going to the further end of the cylinder, in which end there are openings corresponding with those in the slips.

The cylinders are closed by tightly fitting iron doors, and are built into the wall, with furnaces underneath, so arranged as to admit of the accurate regulation of the heat throughout the operation of charring; this occupies with dogwood about 4 hours for R.F.G., and 8 hours for R.F.G^2 gunpowders. The flames surround the cylinder, the heat acting as nearly as possible on its whole surface. The gases and volatilised tar from the wood pass out through the openings in the slip and the corresponding holes in the retort, into pipes communicating with the furnace in which they are burnt; this saves a considerable amount of fuel. When the wood has been sufficiently charred, which is known by the violet colour of the flame from the burning gas, indicating the formation of carbonic oxide, the slip is withdrawn by means of tackling, placed in a large iron case or cooler, covered with a closely fitting lid, and allowed to remain until all the fire is extinguished, which takes about 4 hours; the charcoal is then emptied into smaller coolers, and sent to store. The charcoal is carefully picked over by hand, to ascertain that it all is properly and evenly burnt, and that no rivets from the slips have broken off. It is then kept from ten days to a fortnight in store before being ground, to obviate the danger from spontaneous combustion (caused by absorption of oxygen from the air) to which charcoal is liable when ground directly after burning.

The smaller the cylinders used, the more uniform is the composition of the charcoal produced, since so high a temperature is not needed to carry the heat to the centre of the charge; in the English powder mills, the tendency has been to use small cylinders, some of which hold only 77 lbs. of wood. The use of small cylinders, however, raises the cost of production (Désortiaux).

Violette states that, for the same temperature, a slow carbonisation gives a much higher yield of charcoal than a quick carbonisation; the percentage of carbon being also a little higher in the former case.

Instead of fixed carbonising cylinders, movable cylinders are now used in most black-powder factories. No 'slip' is used, but two cylinders are provided for each furnace, one being charged while a carbonisation is proceeding in the other. The charged cylinders are run into the furnace on rails, which support them over the fire. An elaborate arrangement for the regular distribution of the gases and products of distillation of the wood is used, by means of which they can at will be directed into any one of the furnaces or allowed partially to escape by the chimney.

The principal advantages claimed for this system are homogeneity of the charcoal, the ready regulation of the combustion of the gases by means of the distribution apparatus, and the cooling down of the charcoal out of contact with the air, which does away with the possibility of the charcoal taking fire.

In some English factories, vertical movable cylinders are used, the advantages being that a larger number can be fired at the same time, and the moving of the cylinders into the cooling room is greatly facilitated.

Böckmann mentions that some years ago the use of rotating cylinders was introduced in Sweden; the cylinders being turned 90° about their horizontal axes every half-hour during the carbonisation. It is stated that a more uniform carbonisation is obtained, and fuel saved.

Violette, in 1848, introduced the carbonisation of wood by means of superheated steam. The steam was used at a pressure of ½ to 1 atmosphere, and was raised to the required temperature by being passed through a worm of wrought-iron heated by a fire. For the production (from dogwood) of *charbon roux* containing 70 p.c. carbon, the temperature of the steam had to be about 280°; by using steam heated to about 350°, charcoal containing 77 p.c. carbon was produced, and by heating both cylinder and steam to a temperature not exceeding 450°, charcoal of 89 p.c. carbon was obtained. The charcoal produced by means of superheated steam is remarkably uniform in composition. The method, however, was abandoned, because it gave a larger yield of *charbon roux*, but not of black charcoal, than the ordinary method of carbonisation in cylinders; and the lightly-burnt charcoal was then only required for sporting powder. Also, the cost of production of the charcoal by the superheated steam apparatus was greater.

Güttler, in 1887, invented a process for carbonising wood, especially cuttings and pulp, straw, peat, &c., in heated CO_2. Carbon dioxide is stated to be perferable to superheated steam, on account of the moist state

of the charcoal when cooled in the steam. Gases of combustion, as free as possible from oxygen, are actually used. A producer-furnace is arranged by the side of the charring furnace, in which the CO_2 is produced by blowing air through burning coke by means of a fan. The carbonic acid gas is then blown through a tube into the carbonising cylinder during the carbonising of the wood, &c., and the flow of CO_2 is maintained during the cooling, which in consequence of the presence of the gas may be very rapid.

Composition, &c., of the charcoal.—Carbonising the wood raises the percentage of carbon, diminishing the percentages of hydrogen and oxygen.

Désortiaux states that woods recently cut have almost the same percentage composition; the mean composition of the dried wood being 49·37 p.c. C, 6·14 p.c. H, 43·42 p.c. O and N, 1·07 p.c. ash.

Heintz gives the composition of alder wood *minus* ash, as 48·63 p.c. C, 5·94 p.c. H, 44·75 p.c. O, 0·68 p.c. N. Peterson and Schödler give alder wood *minus* ash as 49·20 p.c. C, 6·22 p.c. H, 44·58 p.c. O and N.

On heating, water, carbon monoxide, carbon dioxide, hydrogen, acetic acid, methyl alcohol, and tar are produced.

Violette found that dogwood was converted into slack-baked charcoal (*charbon roux*) at a temperature of 280°–300°; at 300° the yield (on the small scale) was about 34 p.c., and the composition of the charcoal was 73·24 p.c. C, 4·25 p.c. H, 21·94 p.c. O and N, 0·57 p.c. ash. Between 350° and 400°, black charcoals are produced, the yield being from 31 p.c. to 28 p.c., the composition ranging from about 77 p.c. to 81 p.c. C. Between 1000° and 1250°, the charcoal obtained was very black and hard, the yield was about 18 p.c., and the composition of the charcoal 82·0 p.c. C, 2·30 p.c. H, 14·10 p.c. O and N, 1·60 p.c. ash, at the lower temperature, and 88·14 p.c. C, 1·42 p.c. H, 9·24 p.c. O and N, 1·20 p.c. ash, at the higher temperature.

Experiments made at the Chemical Department of the War Department showed no great difference in the specific gravity of charcoals prepared from willow and alder at 394°–558°; their specific gravity at 15·6° was 1·41 to 1·44. Willow charred at the maximum temperature of 394° for 9½ hours had the composition 79·22 p.c. C, 4·02 p.c. H, 15·32 p.c. O and N, 1·44 p.c. ash, and specific gravity (at 15·6°) 1·414.

The higher the temperature of carbonisation, the less is the inflammability of the charcoal in air, and the greater the thermal conductivity. Violette states that the charcoals prepared from any kind of wood at 300° take fire when heated in the air to 360°–380°; the charcoals from light and porous woods burning more easily than those from hard and close woods. For the same wood he makes the following statement as to the relation between temperature of charring and that of inflammation in air:—

Temperature of charring	Temperature of inflammation
260°–280°	340°–360°
290°–350°	360°–370°
432°	about 400°
1000°–1500°	600°–800°

The lightly-burnt charcoals are much more absorbent of water than those charred at a high temperature.

The charcoals used for the various kinds of Service black gunpowder range in composition from about 75 p.c. C to 86 p.c. C, according to the nature of the powder. All other conditions being the same (viz. proportion of KNO_3, S, and charcoal, size of powder, density, and moisture), the charcoal burnt at lower temperatures (having lower percentage of carbon) gives higher muzzle-velocities and pressures than charcoal burnt at higher temperatures and having higher percentage of carbon; that is, for gunpowder of the composition 75 p.c. nitre, 10 p.c. sulphur, and 15 p.c. charcoal. The greater inflammability of the lighter-burnt charcoal makes the gunpowder, of which it forms part, quicker-burning.

The wood is charred to expel moisture, which would lower the temperature of the explosion products of gunpowder, and to obtain a charcoal of suitable inflammability.

Appended is a table of the percentage composition of some charcoals from gunpowders of Waltham Abbey make, and of a sporting powder, which will serve as types of the charcoal used in the different kinds of black gunpowder:—

—	W. A. Pebble	W. A. Rifle Large Grain	W. A. Rifle Fine Grain	W. A. Fine Grain	Curtis & Harvey Sporting
C . .	85·26	80·32	75·72	77·88	77·36
H . .	2·98	3·08	3·70	3·37	3·77
O (and N)	10·16	14·75	18·84	17·60	16·62
Ash . .	1·60	1·85	1·74	1·15	2·25

(Noble and Abel, Phil. Trans. 1880, 171, 218).

Pulverising, mixing, and incorporating the ingredients.—At Waltham Abbey, the refined nitre is used for gunpowder without being previously dried or ground, but the moisture is estimated and allowed for. The charcoal is ground in a mill; the grinding is done by a cone working in a cylinder, both being suitably toothed. The ground charcoal is made to pass through a spout into a revolving reel of 32-mesh copper-wire gauze, 8½ feet long and 3 feet in diameter, inclined at an angle of about 4° to the horizontal, and making 38 revolutions per minute. The charcoal which passes through the gauze is fit for use, and is collected in a closed reel case; the charcoal too coarse to pass through the gauze falls through the further end of the reel into a vessel, and is reground. The sulphur is ground under a pair of iron edge runners, a smaller-sized incorporating mill, and is sifted through a reel similar to that used for the charcoal. Precautions are taken to connect the sulphur mill to earth, in order to allow the electricity generated by the rubbing of the sulphur to escape.

The ground ingredients are carefully weighed out in their proper proportions; the largest charge worked in the incorporating mill is 80 lbs. The charge receives a preliminary mixing in the

mixing machine, a cylindrical drum of gun-metal or copper, about 2 feet 9 inches in diameter and 1 foot 6 inches wide. An axle bearing 8 rows of gunmetal 'flyers' or fork-shaped arms passes through the centre of the drum; the drum and arms are made to revolve in opposite directions, the former making about 40 revolutions per minute, the latter 120. The mixing occupies five minutes, the mixture being then hand-sifted through an 8-mesh copper-wire sieve over a hopper, to remove foreign substances; the 'green charge' is then tied up in a bag ready for the incorporating mill.

The incorporating mill consists of a circular iron bed, about 7 feet in diameter, very firmly fixed in the floor of the building, on which two iron cylindrical edge runners revolve. The iron runners are 6½ feet in diameter, 15 inches wide, and weigh about four tons. They have a common axle resting in a solid cross-head attached to a vertical shaft, which passes through a bearing in the centre of the bed, and is in gear with the machinery.

The bed has a sloping outside rim. The runners are at an unequal distance from the axis, the eccentricity being equal to half the thickness of a runner; they thus work the charge in the inner and the outer part of the bed, their paths overlapping. The runners are followed by two 'ploughs' of wood, covered with leather, attached to the cross-head by arms; one plough works near the vertical shaft, the other near the rim of the bed, throwing the composition under the runners.

The green charge is spread evenly on the bed of the mill by means of a wooden rake; it is damp with the moisture of the nitre, but an additional quantity of distilled water (2 to 7 pints) is added from time to time, according to the state of the atmosphere; the moisture assists the incorporation, and the charge is kept not too dry or it would be scattered as dust, not too wet or it would slip away from the runners or cling to them.

The iron runners make 8 revolutions per minute, the green charge is worked under them for 4 hours for R.F.G. powder, for 7 to 8 hours for R.F.G^2 powder, and for 3 hours for R.L.G^2 and R.L.G^4. Dust and reworked charges are worked for 40 minutes.

A drenching apparatus is placed over the bed of each mill, by means of which, in case of an explosion, a tank of water is overturned and the charge drowned. This is done by the action of the explosion gases on a flat wooden lever arrangement, pivoted, and attached to the tank. By means of a horizontal shaft connecting all the levers of a group of mills, an explosion in one mill drowns all the others.

The short radius of the circular path traversed by the runners causes them to take a twisting as well as a rolling motion, and gives them a combined crushing and grinding action very favourable to the thorough trituration and incorporation of the ingredients.

The 'mill-cake,' as the worked charge is called, should have a uniform appearance, and should contain 1 p.c. to 3 p.c. moisture for small-arm powders, 3 p.c. to 6 p.c. for the larger-grained powders.

Breaking down the mill-cake and pressing. —The mill-cake is next reduced to meal, for convenience in charging the press-box, and in order that the powder may be uniformly pressed. The mill-cake is broken down by means of two pairs of gun-metal rollers, the upper pair being grooved and placed directly above the other pair, which are smooth. The rollers revolve towards each other, dangerous friction from the accidental presence of any hard substance being prevented by one roller of each pair working in sliding bearings connected with a weighted lever causing a pressure of about 56 lbs., so that the rollers would open at any greater pressure. The rollers are fed with mill-cake from a hopper (placed at one end of the machine, below the level of the upper pair of rollers), by means of an endless band of canvas 2½ feet wide, with cross strips of leather sewn on at intervals of about 4 inches. The band passes over a roller at the bottom of the hopper, and over another placed above the upper pair of rollers; on being set in motion it carries the cake from the hopper to a point from which it falls on to the first pair of rollers; the crushed cake then falls on to the second pair, by which it is reduced to meal. It falls into wooden boxes, and is transferred to a magazine ready for pressing.

The meal is pressed into cake by a hydraulic press, fed from an accumulator, the head and bed-plate of which are made of cast iron or cast steel. The powder is pressed between plates about 1 foot 8 inches by 2 feet 4 inches and about ⅝ inch thick. Formerly brass plates were used, but now ebonite plates are usually preferred, because they are not so easily bent out of shape, and also because they have sufficient elasticity to transmit the pressure evenly all over the layer of powder, even if they should get out of the horizontal. They have the disadvantage of becoming easily electrified; in fact, alternate layers of ebonite and powder really form an electric pile. To obviate any danger from the possible accumulation of electricity, the presses are provided with an earth connection.

In charging the press, a plate is first put on to the carriage, and round this is placed a wooden frame, deeper than the thickness of the plate. This frame is filled with powder, and the surface smoothed by means of a flat lath, and a second plate placed on the top. The frame is then lifted to the level of the second plate, and the process repeated until the whole charge is made up. A pressure of between 375 and 450 lbs. per square inch is applied, according to the fineness of the powder, the amount of moisture it contains, the state of the atmosphere, and the density required. The pressure is slowly applied, eased off and reapplied several times in order to obtain great density without using excessive pressures: the compression usually lasts from 30 to 40 minutes. A pressure of 375 lbs. per square inch applied for from 1½ to 2 hours produces a cake with an average density of 1·7 to 1·8. The centre of the cake has, however, a greater density than the edges; the edges of the cake are on that account cut away to the extent of about an inch. The amount cut away need not exceed 10 p.c. The centre layers of the pile are slightly less compressed than the top and bottom layers, but these differences in density are partly removed by the subsequent operations. The layers of pressed

cake are broken into pieces with a wooden mallet and put into barrels.

Granulating.—The press-cake is converted into grain by means of a machine consisting of three or four horizontal pairs of gun-metal rollers in a gun-metal frame. The pairs of rollers are placed one above the other, on an axial line inclined at about 35° to the horizontal, the vertical distance between the pairs of rollers being about 2½ feet. For fine-grain powders, the highest pair of rollers has teeth ½ inch apart, the next pair has ¼ inch teeth, and the two bottom pairs have no teeth. Like those of the breaking-down machine, the rollers work in sliding counter-weighted bearings; they make about 25 revolutions per minute. The machine is fed with press-cake from a hopper by means of a moving endless band. Short screens, covered with copper-wire gauze (10-mesh for small-arm powders), are placed under each pair of rollers except the bottom pair, so that the powder too large to pass through the gauze passes on from one pair of rollers to the next. Beneath the short screens are placed two long screens in an inclined position, the upper one of 10-mesh, and the lower one of 20-mesh copper gauze fixed in a frame. A rapid, longitudinal, vibratory motion is imparted to all the screens while the machine is working, to assist the sifting and the flow of the powder. The grain that passes through the short screens will fall through the 10-mesh long screen. That which is retained on the 20-mesh screen is R.F.G. or R.F.G^2 powder; it falls into boxes made to move forward as they are filled. The grains too large to pass through the short screens fall into separate boxes, and are transferred to the hopper to be passed again through the rollers; while the fine powder which passes through the 20-mesh sieve falls on to the wooden bottom of the frame and is collected separately, to be sent back to the incorporating mill for a short re-working.

For granulating R.L.G^2 and R.L.G^4 powders, three pairs of rollers are usually employed, the two upper pairs with larger teeth, the bottom pair smooth. The grain from the granulating machine is called "foul grain." By granulating a gunpowder there is no danger, as there would be with a dust, of segregation of the ingredients during transport according to their densities, the powder is less hygroscopic, there is less danger of escape from storing vessels, and the inflammability of the powder is increased, since the flame can penetrate more quickly through the charge.

Dusting and glazing.—R.F.G. and R.F.G^2 powders are freed from dust after granulation by being passed through a dusting-reel. This is a cylindrical frame about 8 feet long and 1½ feet in diameter, covered with 20-mesh copper-wire gauze, and set at a very small angle with the horizontal. The reel is enclosed in a case to catch the dust, but is open at both ends; it is fed continuously at the upper end with powder from a hopper, while the reel makes about 40 revolutions per minute. The powder falls from the lower end of the reel into barrels.

The polish given to the powder grains by glazing is of advantage in diminishing the tendency of the powder to absorb moisture, by breaking off any sharp angles and points, and stopping up the outer pores of the grain, and in enabling it to bear transport without going to dust. Glazing also increases the density of the powder; a powder with a density of, for example, 0·810 before glazing having its density progressively increased to 0·893 after 42 hours' glazing. The small-arm powders, R.F.G. and R.F.G^2, are glazed in large drums—cylinders 2 feet wide and 6 feet in diameter (a pair of drums on one axle) making about 12 revolutions per minute. The drums each take about 900 lbs. of powder; they are run 5½ hours for R.F.G., and 10 hours for R.F.G$_2$. No graphite is used for these powders; the friction and heat caused by the motion suffice to produce a brilliant glaze. The glazed powder receives another dusting in a reel covered with 20-mesh wire-gauze, and is then sifted through an 11-mesh sieve into barrels. R.L.G^2 powder is run for 1½ hours in drums as above, with about one ounce of graphite per 100 lbs. powder. R.L.G^4 is glazed for 3 hours in the old pattern glazing barrels, the same proportion of graphite as for R.L.G^2 being added after the barrels have run for 2 hours. Each barrel takes about 400 lbs. of powder; they are 5 feet long by 2½ feet diameter of ends, and make 34 revolutions per minute. The graphite increases the gloss of the powder, and the powder is also rendered less hygroscopic through the increased density of the surface layer.

Drying, finishing, blending.—The next operation is drying, which is carried out in a drying room heated by steam pipes. The gunpowder is placed in wooden frames about 3 feet × 1½ feet × 2½ inches with canvas bottoms, each holding about 12 lbs. of powder, and placed on open framework shelves with which the room is fitted, seven or eight tiers of shelves rising one above another, the steam pipes running under them. The moist air of the room is constantly changed by means of ventilators. At Waltham Abbey, about 50 cwts. of gunpowder are dried at one time. The time and temperature of drying varies with the kind of powder and the amount of moisture in it, the length of time and the temperature increasing with the size of the grain. Thus, R.F.G. requires 1 hour, and R.F.G^2 2 hours at 38°, R.L.G^2 2 hours at 43°, and R.L.G^4 6 hours at 46°. Another system of drying is to drive a current of cold air over steam-heated coils into the drying-room or stove by means of fans. In some factories, a current of cold air is used, after being freed from its moisture by means of calcium chloride, caustic lime, or strong sulphuric acid; and drying at ordinary temperatures *in vacuó* has also been tried. The drying should be done evenly and not too rapidly, so that the pores of the powder are not opened too quickly.

Rapid drying, too, has a tendency to cause the larger-grained powders to crack, and sometimes causes an efflorescence of nitre on the surface of the grains.

The dried powder is *finished* by being rotated in a horizontal reel—a long cylindrical wooden frame covered with canvas, making 45 revolutions per minute—the fine-grain being reeled longer than the large-grain powders. Finishing frees the powder grains from the small amount of dust produced in the process of

drying, and gives them (and especially to small-arm powders) a final glaze.

Before-drying, and again after finishing, a uniform blend or mixture is made of a large number of barrels of gunpowder. Advantage is taken of every opportunity, in the processes of the manufacture of gunpowder, to mix or 'blend' the grain together so as to obtain more uniform results at proof. This is done by means of a wooden hopper divided into four equal compartments, each able to hold a barrel of gunpowder; the compartments can be emptied simultaneously into a central shoot by means of openings with sliding shutters in the bottom of each. This method of blending, especially with the smaller sizes of grain, is found to give batches of powder with very uniform firing results.

Pebble and prismatic powder. These cut and moulded powders are no longer manufactured, as smokeless powder is now used even for guns of the largest calibre, but a short account of them is given, owing to their great historical interest. The use of pebble powder in this country dated from about the year 1865. Rodman had previously shown that in the gun the pressure diminished as the size of the grains of gunpowder increased, and that the velocity of the projectile could at the same time be maintained by an increased weight of charge.

Pebble powders (P, cubes of $\frac{5}{8}$-inch; and P^2, $1\frac{1}{2}$-inch cubes) were used for larger guns than were the rifle large-grain powders. Up to the formation of the press-cake, the processes of manufacture were, with some variations, the same as for the finer-grained powders.

The *P powder* was cut from the press-cake, which was pressed into slabs of about 15 inches by 30 inches, and of the required thickness. The cutting machine consisted of two pairs of phosphor-bronze rollers, having longitudinal knife-edges with spaces between them corresponding to the required size of the powder. The first pair of rollers cut the press-cake into strips, which were fed on endless bands to the second pair of rollers, set at right angles to the first, which cut the strips into cubes. These cubes were allowed to fall into a dusting reel, with copper-wire meshes but little smaller than the cubes.

P^2 powder was cut by hand from the press-cake by means of lever-knives of gun-metal—knives hinged at one end, with a handle at the other. The press-cake was first cut into strips and then across into cubes.

Both P and P^2 powders were run in the glazing barrels, by which treatment the edges and corners of the cubes were rubbed down, and a harder surface produced. The powders were then dried at 54°, which required a very much longer time than for the smaller-grained powders; a finishing process followed, the powders being run in wooden barrels with ribs wide enough apart to combine sifting with the finishing glazing. A small quantity of graphite was introduced into the barrels towards the end of the finishing process.

Prismatic powder. This may be regarded as a modification of the perforated cake powder devised by Rodman in 1860. The latter powder consisted of cakes of powder compressed by the hydraulic press, of the diameter of the bore of the gun, and pierced longitudinally with holes of about $\frac{1}{4}$ inch diameter, the cakes being packed in the cartridge so that the holes should correspond. Rodman was led to introduce this form of powder by the consideration that, with solid grains of gunpowder, the surface undergoing combustion in the gun diminishes as the combustion proceeds, and that consequently the strain on the gun is greatest in the earlier stages of the combustion. In the case of the perforated cake gunpowder, as the combustion progressed in the longitudinal holes, the surface undergoing combustion increased. Rodman's theoretical views were confirmed by experiment, but the liability of the perforated cake powder to break up by carriage or when handled, led to its replacement by much smaller hexagonal prisms with one central cylindrical hole; the prisms used in this country were about 1 inch high, the distance between opposite sides of the hexagon about 1·37 inches, the central hole about 0·4 inch in diameter. They were used for heavy breech-loading guns, and were packed so as to form rigid cartridges.

The prisms were pressed from a moderately large-grained powder granulated from press-cake freed from dust in the ordinary way, but not glazed, and finally dried and blended. The increased density of the powder due to the compression delayed the burning and reduced the initial pressure in the gun.

Brown or cocoa gunpowder. The introduction of this powder was a great innovation in powder making, as it greatly improved the shooting of big guns and allowed the use of guns of still larger calibre than even the black prismatic powder. It was composed of 79 p.c. nitre, 3 p.c. sulphur, and 18 p.c. charcoal per 100 of dry powder, and contained ordinarily about 2 p.c. moisture. The 'charcoal' also was a very lightly baked material, the percentage of carbon contained in it being but little higher than that in the (dry) wood or straw from which it was made.

This powder was used for heavy breech-loading guns in the form of hexagonal prisms, having the same dimensions as the black prismatic powder. The rate of ignition and of combustion of the brown prismatic powder was slower than that of the black, and for equal muzzle velocities of the projectile it produced less pressure in the powder-chamber of the gun than black powder, and gave a thinner smoke than the latter.

Brown or cocoa powder gives on explosion a greater quantity of heat and a smaller volume of permanent gases than does an equal weight of black gunpowder; but the larger amount of water vapour in the products of explosion of brown powder have an important influence in lowering temperature. The products of explosion of brown powder undergo considerable dissociation at first, thus lowering the initial pressure in the gun, and subsequent recombination, and so giving sustained pressures as the projectile moves along the bore. The more gradual development of the pressure and the reduction of the maximum pressure increased the life of the gun and rendered the use of lighter guns possible.

Sporting powder. Considerable quantities

of black gunpowder are still used for sporting purposes. The proportions of the ingredients vary slightly from those used for military powders, in order to produce the desirable qualities of quick ignition and combustion. The ease of ignition of a black powder does not vary much with the composition, but an excess of charcoal quickens, whilst an excess of nitre slackens, the rate of combustion. To increase the rapidity of combustion, a slack-burnt or red charcoal is usually used instead of black. The composition of the sporting powder of several countries is given in the following table:—

Composition of Black Powder used for Sporting Purposes.

—	Potassium nitrate	Sulphur	Charcoal
England . .	75·0	10·0	15·0
France . .	78·0	10·0	12·0
Germany . .	78·0	10·0	12·0
Austria-Hungary.	76·0	9·5	14·5
Switzerland .	78·0	9·0	13·0

The powders are of high grade and carefully made by processes practically identical with those used in the manufacture of military powders. Occasionally there are modifications, such, for instance, as the use of drums instead of mills for powdering and mixing the ingredients, because the charge can be less moist and the mixing more rapid, so that better incorporation results in a given time, with resultant greater regularity in shooting.

Mining and blasting powder. The chief requirements of blasting powder are that it should be cheap and develop as large as possible a quantity of gas at a high temperature. The usual composition of blasting powders in various countries is:—

Composition of Black Powder used for Mining and Blasting Purposes.

—	Potassium nitrate	Sulphur	Charcoal
England . .	75·0	10·0	15·0
France . .	72·0	13·0	15·0
Germany . .	70·0	14·0	16·0
Austria-Hungary.	60·0	18·5	21·5
Italy . .	70·0	18·0	12·0
Russia . .	66·6	16·7	16·7

These proportions are by no means rigidly adhered to. Thus, in England, blasting powders varying from the above proportions to—potassium nitrate 65, sulphur 20, charcoal 15,—are made. Other compositions especially made for use in fiery mines will be mentioned later under 'Black powder safety explosives.'

Blasting powder is a large-grained powder, sometimes coated with graphite, compressed into cartridges by means of a hydraulic press. As will be mentioned further on, while the mining powder with low nitre and high sulphur gives on explosion a larger volume of permanent gases, it gives a much smaller quantity of heat than black gunpowder.

Fuse powder. A gunpowder of special quality and constant composition is now manufactured for use in 'safety and other fuses. Formerly, siftings from mining powder were frequently used, but this caused unevenness in burning and was frequently the cause of accidents through 'hang-fires.' It is a mealed powder; that is, of very fine granulation, but free from dust.

Properties and products of explosion.—The '*density*' (as determined by Bianchi's densimeter) of the different kinds of gunpowder mentioned ranges from about 1·67 in the case of R.L.G[2] to about 1·87 in the case of brown prismatic powder. Increase of density of a gunpowder causes its slower combustion, and (under comparable circumstances) diminishes the muzzle velocity of the projectile and the pressure in the gun.

Increase of the amount of moisture in a gunpowder causes diminished temperature of the products of explosion, and lessens the muzzle velocity of the projectile and the pressure in the gun.

Black gunpowder can be *ignited* by a blow or by an increase of temperature: it explodes at about 300°. The exploding temperature was taken by heating small grains of the gunpowder buried in the sand of a small deep sand-bath, in which the bulb of a Geissler pressure mercurial thermometer was immersed. Black prismatic gunpowder inflamed at about 290°, brown prismatic at 304°. At a temperature slightly above 100° the sulphur can be completely volatilised out of the powder without inflammation taking place. Violette determined the ignition-point by projecting the powder on to molten tin kept at different temperatures. He found that all classes of gunpowder after powdering fired at from 265° to 270°, and that the firing-point depends but little on the composition, but that the size and shape of the grain and the perfection of the incorporation affected the results; thus, blasting powder in grains fired at 270° and extra fine sporting powder at 320°.

The ignition of gunpowder is more difficult and the rate of combustion diminishes with diminished atmospheric pressure. In an atmosphere maintained at a pressure of about 0·5 inch mercury, gunpowder is not exploded by contact with a platinum wire heated to redness by an electric current; the grains in contact with the wire fuse, and, if the passage of the current be maintained, burn slowly without causing the explosion of the remainder. Under the high pressures produced in a gun when fired, the velocity of combustion of gunpowder very rapidly increases.

The *products of the combustion* of gunpowder have been examined by several chemists, of whom Gay-Lussac (1823), Chevreul (1825), Bunsen and Schischkoff (1857), Karolyi (1863), Federow (1868), Noble and Abel (1875–80), may be more particularly mentioned.

The investigation of the subject by Noble and Abel is much more complete than the others, and some of their results will be briefly mentioned.

The *quantity of heat* evolved by the explosion of gunpowder was determined by firing 10 to 26 grams of gunpowder in strong steel explosion vessels of 32 and 119 c.c. capacity respectively, the explosion vessels being surrounded by water in a calorimeter of the usual kind.

The *volume of permanent gases* produced was determined by exploding in closed steel

vessels, having an internal capacity of about one litre, quantities of gunpowder varying in weight from about 100 to 800 grams. The vessels retained the whole of the products of explosion, and were provided with an arrangement by which the gases could be allowed to escape, and could be collected or measured. The pressure in the vessels was measured by means of the usual crusher-gauge (piston acting on, and compressing, a small copper cylinder) contained in a plug screwed into the vessel.

The *pressures* in the explosion vessels varied with the density of charge $\left(\frac{\text{volume of powder}}{\text{capacity of vessel}}\right)$. With a density of charge of 0·3, the pressure observed was about 5 tons per square inch; with 0·7 density, the pressure was about 20 tons; with density 1, the pressure was about 42 tons; and with density 1·2, the pressure was about 56 tons.

The powders experimented with had the following percentage composition; the first three were of Waltham Abbey make:—

Nature of powder	Potassium nitrate	Potassium sulphate	Potassium chloride	Sulphur	Carbon	Hydrogen	Oxygen	Ash	Water
Pebble powder	74·67	0·09	—	10·07	12·12	0·42	1·45	0·23	0·95
Rifled large-grain R.L.G.	74·43	0·13	—	10·09	12·40	0·40	1·27	0·22	1·06
Fine-grain	73·55	0·36	—	10·02	11·36	0·49	2·57	0·17	1·48
Sporting powder	74·40	0·29	trace	10·37	10·66	0·52	2·29	0·31	1·17
Mining powder	61·66	0·12	0·14	15·06	17·93	0·66	2·23	0·59	1·61
Spanish spherical powder	75·30	0·27	0·02	12·42	8·65	0·38	1·68	0·63	0·65
Cocoa powder	78·83	—	—	2·04	Charcoal 17·80				1·33

The composition of the solid and gaseous products of the explosion of these gunpowders is given in the following table; the numbers given for the first three powders are the means of 9 experiments with density of charge from 0·1 to 0·9; the sporting and mining powders had density of charge 0·3, the Spanish spherical, 0·7:—

PERCENTAGE COMPOSITION BY VOLUME OF THE DRY PERMANENT GASES.

——	Pebble	R.L.G.	Fine-grain	Sporting	Mining	Spanish spherical	Cocoa
Carbon dioxide	48·95	49·29	50·62	50·22	32·15	53·34	51·30
„ monoxide	13·63	12·47	10·47	7·52	33·75	4·62	3·42
Nitrogen	32·16	32·91	33·20	34·46	19·03	37·80	41·71
Hydrogen sulphide	2·60	2·65	2·48	2·08	7·10	2·74	—
Methane	0·31	0·43	0·19	2·46	2·73	—	0·31
Hydrogen	2·35	2·19	2·96	3·26	5·24	1·29	3·26
Oxygen	—	0·06	0·08	—	—	0·21	—

PERCENTAGE COMPOSITION BY WEIGHT OF THE DRY SOLID RESIDUE.

——	Pebble	R.L.G.	Fine-grain	Sporting	Mining	Spanish spherical	Cocoa
Potassium carbonate	59·26	61·05	51·88	59·10	41·36	35·66	$KHCO_3$ 13·55 K_2CO_3 64·12
„ sulphate	12·93	15·10	22·71	21·65	0·59	48·55	22·33
„ monosulphide	18·98	14·46	18·16	12·42	37·10	7·72	none
Sulphur[1]	8·08	8·74	6·90	6·45	14·11	7·04	—
Potassium thiocyanate	0·25	0·22	0·13	—	2·95	0·04	—
„ nitrate	0·24	0·27	0·17	0·29	0·09	0·95	trace
Ammonium sesqui-carbonate	0·10	0·08	0·05	0·09	1·78	0·04	trace
Charcoal	0·16	0·08	—	—	2·02	—	—

The cocoa powder gives a completely oxidised saline residue, and the proportion of incompletely oxidised gases is smaller with this powder than with the others.

The quantity of heat (in gram-degree units), and the volume (at 0° and 760 mm.) of the permanent gases, per 1 gram of dry powder, were found by Noble and Abel to be:—

——	Units of heat	Cubic centimetres Permanent gases
Cocoa	837·0	198·0
Spanish spherical	767·3	234·2
Sporting	764·4	241·0
Fine-grain	738·3	263·1
R.L.G.	725·7	274·2
Pebble	721·4	278·3
Mining	516·8	360·3

[1] Present in the residue as higher sulphide of potassium.

It will be seen that the order of decrease of units of heat is that of increase of volume of permanent gases; and Noble and Abel observed that the products of heat-units by gas volume do not differ greatly from a constant value, that this points to the conclusion that the pressures at any given density of charge, and the power of doing work of the various powders, are not very materially different,—a conclusion verified by experiment for the three Waltham Abbey powders, and in a less degree also for the other powders. The total potential energy of gunpowder they estimated at about 340,000 kilogram-metres per 1 kgm. of powder, or a little under 500 foot-tons per 1 lb. This calculation supposes the infinite expansion of the products of combustion, but they estimated the actual energy of gunpowder realised by modern guns as varying from about one-tenth to one-fifth of the total theoretical effect.

The *temperature* produced by the explosion of gunpowder they estimated at about 2,100° in the case of the pebble or R.L.G. powder, at about 2,200° in that of the Spanish pellet powder (Noble and Abel, Trans. Roy. Soc. 1875, 1880; Noble, Heat-Action of Explosives: a Lecture to Inst. Civil Eng. 1884).

Debus, in 1882, first showed that potassium disulphide is a product of the combustion of black powder. He considered that the combustion takes place in two stages, at first an oxidation, with the formation of potassium sulphate and carbonate, carbonic acid gas, free nitrogen, and, perhaps, carbonic oxide; and, secondly, a reduction in which free carbon and sulphur reduced the potassium sulphate and carbonate.

Debus also showed that from the percentage composition of the powders fired and the products of combustion, the combustion of the powder, as an end result, could be represented in the form of an ordinary equation, from which the theoretical work obtainable from the powder can be calculated (Debus, Annalen, vols. 212, 213, 265, and 268).

Examination of gunpowder.—The powder, examined by the eye, should have a perfectly uniform colour, depending on its composition and a proper amount of glaze. Small white specks on the surface of the grains indicate that the nitre has effloresced during drying. The grains must be compact, not flat, in shape; and their size must be uniform, as tested by sifting; and free from dust, as shown by the powder leaving no mark on running it over a sheet of paper. The grains must be hard and crisp, as judged by crushing in the hand. The thoroughness of the incorporation is tested by 'flashing' a small measured quantity of the powder on a porcelain tile by means of a hot wire. The 'flash' should show but few sparks, and there should be no residual solid matter.

By the *density*, or *real density*, of a powder is understood the specific gravity of the grains or prisms, including the air contained in their pores. It is usually determined by the Bianchi densimeter. 100 grams of the sample, crushed, if necessary, but free from dust, are weighed out and transferred to the globe of the densimeter. This removable glass globe is fitted with stopcocks above and below, the upper is attached to an air pump, the lower connected by means of a tube with a vessel of mercury, the density of which is known, at the temperature, usually 60°F. or 70°F., to which it is adjusted. The lower stopcock is closed, the globe exhausted, the stopcock opened, and the mercury then allowed to rise to the height which the atmosphere will support, the lower stopcock closed again, and the upper part of the apparatus opened to the air by means of the air-pump gauge stopcock. The operations are repeated, the mercury surrounding the powder grains being thus subjected to two atmospheres pressure. The globe is then closed, unscrewed, and weighed. Then if S = density of mercury at temperature of determination, W = weight of globe filled with mercury, and W_1 = weight of globe filled with powder and mercury; density of sample

$$= \frac{S \times 10}{(W - W_1) + 100}.$$

Hygrometric test.—All kinds of black powder are liable to absorb more or less moisture from the air, depending on the quality of their charcoal and saltpetre. The tendency any powder has to absorb moisture is determined by exposing it for a given time—24 hours for the smaller powders—in a specially insulated box at a recorded temperature, to air saturated with moisture, from a saturated solution of saltpetre. The increase in the weight of the powder, added to its previous moisture content, is taken as a measure of its 'hygrometric quality.' The results are, however, not very reliable.

Analysis.—*Moisture* is determined by loss, on the coarsely powdered sample, after 1 hour at 70°, or preferably by exposure over sulphuric acid until of constant weight.

The *nitre* is determined by extraction with warm water, filtering, and evaporating the solution in a platinum dish. The final washings should be kept separate, as the charcoal has a tendency to come through the filter, evaporated to dryness and again extracted, when the filtrate is clear and is added to the bulk. The nitre is dried at 280°, cooled and weighed.

The *sulphur* is estimated by heating 1 gram of powder in a beaker with strong nitric acid until the action moderates, cooling a little, adding a little potassium chlorate to complete the oxidation, and evaporating to dryness. The residue is treated with strong hydrochloric acid, and again evaporated to dryness. The residue is taken up with water (any insoluble matter, grit and graphite, being filtered off and weighed), and the solution precipitated with barium chloride, &c., as usual.

The *charcoal.*—The nitre is removed from the gunpowder by treatment with water, the charcoal and sulphur filtered off, dried, powdered, and treated with carbon disulphide to remove sulphur. The dried charcoal still retains a small quantity of sulphur, which is estimated by the method given above, after the charcoal has been dried in hydrogen in the same manner as for a combustion. The weight of sulphur is, of course, deducted from the weight of charcoal used for the combustion. About 0·5 gram of charcoal is taken for combustion; it is dried (in the boat in which it is to be burnt) by heating for 15 minutes to 170°, in the case of a black charcoal, in a current of hydrogen. The charcoal is allowed to cool in the current of hydrogen, and is transferred to an air-pump

receiver, which is then exhausted. The boat with the charcoal is weighed in a closed tube. The combustion is made in oxygen, a length of granulated copper oxide, maintained at a red heat, being in front of the boat; and in front of the oxide of copper is a shorter length of lead chromate, heated to very low redness to absorb SO_2 or SO_3: in other respects, the combustion is made as usual.

Other Potassium Nitrate Mixtures.

Sulphurless gunpowder of various compositions has frequently been tried for special purposes, but without much success. Sulphur renders a powder easy of ignition and increases its rate of burning, and its inclusion is practically essential. Sulphurless powder, moreover, has a tendency to crumble to dust on storage or handling.

Antimony sulphide has been proposed as a substitute for sulphur in black powder, but it is only in certain detonating compositions that it is actually used.

Many combustible substances, amongst others coal, coke, peat, sawdust, bark, bran, tan, sugar, starch, dextrin, gum, hydrocarbons such as paraffin and naphthalene, ferro- and ferricyanides of potassium, tartaric acid, Rochelle salt, sodium acetate, &c., have been proposed and patented as substitutes for all or part of the charcoal in nitrate mixtures. Many of these substances are substituted in order to reduce the amount of smoke. They almost invariably reduce the inflammability of the powder, slacken its combustion, and leave a larger amount of residue, but frequently give off larger quantities of gas. These mixtures were suggested principally as blasting explosives, and many were authorised for manufacture in this country, but at the present time their use is practically confined to the Continent.

A few of these explosives will suffice:

Fortis was a mixture of nitre, tan, and sulphur, with small quantities of iron sulphate and glycerol, and it was claimed that nitroglycerin was produced during explosion in a blast hole, with consequent increase of power.

Carbonite, as introduced by Hellhoff of Berlin, was a mixture of nitrobenzene, potassium nitrate, sulphur, and kieselguhr; said to be plastic enough to fill a bore hole, to be non-explosive by blows, when inflamed to burn away quietly without explosion, and when detonated to have the same explosive force as kieselguhr dynamite. It has been used in coal-mines in Germany, but modern carbonites contain nitroglycerin, and are mentioned under 'Dynamites.'

Carboazotine was a mixture of nitre, lamp-black, sawdust, and sulphur, with a little iron sulphate. This explosive required compression into cartridges before it would explode.

Petrolite, as manufactured in Hungary, is a mixture of nitre, wood pulp, coke-dust, and sulphur.

Jahnite, as made in Austria, is a mixture of nitre, lignite coal, and sulphur, with very small quantities of picric acid, potassium chlorate, and calcined soda.

Amidogène, a similar mixture to the last, contained nitre, charcoal, bran, or starch, and sulphur, with a little magnesium sulphate. This powder had a very slow rate of combustion, but developed large quantities of gas. It was used on a large scale for blasting operations at the Iron Gates on the Danube, and in coal-mines.

Black Powder Safety Explosives.

Ordinary black gunpowder is unsuitable as a blasting agent for use in fiery mines, and its use is everywhere prohibited for this purpose. Many modifications of gunpowder have been tried, and several mixtures have been manufactured which were able to pass the official tests. A few of these mixtures are:—

Argus powder, which contained 81 p.c. potassium nitrate, 18·5 p.c. charcoal, containing 30 p.c. of volatile matter, and 0·5 p.c. sulphur.

Earthquake powder, which contained 79 p.c. nitre, and 21 p.c. charcoal, containing 56 p.c. volatile matter.

Elephant-brand powders, which had the composition of ordinary gunpowder, but No. 1 was fired with 6 inches of ammonium oxalate, and No. 2 with 6 inches of sodium bicarbonate, in front of the cartridge.

Oxalate blasting powder, which was composed of 71 p.c. nitre, 14 p.c. charcoal, and 15 p.c. ammonium oxalate.

All these explosives were subsequently removed from the 'permitted' list.

Bobbinite, manufactured by Curtis and Harvey, is still on the 'permitted' list, and was the most extensively used of all safety explosives in this country in 1909. It is really a high-grade gunpowder, containing but little sulphur, with added ingredients to increase the safety. As originally made, it consisted of 64 p.c. nitre, 2 p.c. sulphur, and 19 p.c. charcoal, with 15 p.c. of a mixture of ammonium sulphate and copper sulphate. In a later composition the mixture of ammonium and copper sulphates was replaced by 8 p.c. of starch and 3 p.c. of paraffin wax, the other ingredients being correspondingly increased. The mixture is compressed into pellets, which are coated with paraffin wax.

Bobbinite is safe to handle, and is fired without detonators; it is slow burning, and does not break up the coal so much as most safety explosives. A Home Office Committee was appointed in 1906 to investigate the alleged danger of 'bobbinite' in fiery mines, but it concluded that these fears were groundless, and the manufacture and use of the explosive was still permitted. The committee also concluded that the damage with 'bobbinite,' as with other explosives, was greater when the shots were not efficiently stemmed.

Sodium Nitrate Mixtures.

Sodium nitrate has a higher percentage of available oxygen than potassium nitrate, and is also cheaper, but its hygroscopicity is a great drawback to its use in powders intended for keeping a long time. In dry climates the sodium nitrate powders, made as required for consumption, have been used, as they effect a saving, and are more powerful than the corresponding nitre mixtures. A sodium nitrate mining powder was used, for instance, on a large scale and with considerable economy in the Suez Canal works; but such mixtures are no longer manufactured, except in Austria-Hungary.

The replacement of the potassium nitrate of black gunpowder by an equivalent quantity of

sodium nitrate would give, according to Berthelot's calculation, if the chemical reactions were exactly the same in the two cases, a slightly greater quantity of heat and a larger volume of gases.

Mixtures containing sodium nitrate do not ignite so readily, and burn more slowly than those containing the potassium salt.

The hygroscopic properties of sodium nitrate are chiefly due to traces of nitrates and chlorides of calcium and magnesium, which it is impossible to eliminate on a commercial scale; chemically pure sodium nitrate being only slightly deliquescent. In recent years, it has been proposed to add a small quantity of oil, or liquid, or molten solid hydrocarbon, to sodium nitrate explosives, in order to coat the particles of nitrate, and so prevent the absorption of moisture.

Sodium nitrate has been used, or proposed, in mining powders, either alone or in partial substitution of the potassium nitrate, with practically all the numerous combustible substances given under 'other potassium nitrate mixtures.' For example, one of the early forms of '*carbonite*,' made by Schmidt and Bichel of Schlebusch, consisted of 9–10 parts of sodium nitrate, 1 part of sulphuretted tar oil, and 0·5 part of nitrocumene.

Barium Nitrate Mixtures.

Barium nitrate contains a smaller percentage of available oxygen than potassium nitrate, but, owing to its higher specific gravity, it contains more oxygen, bulk for bulk, than the latter salt, and from this point of view should be more valuable in disruptive explosives. It also has the advantage that it is the least hygroscopic of all the nitrates used in explosives, but its higher price is against its use. Explosives containing it have a higher ignition-point and are slower burning than those containing potassium nitrate.

Barium nitrate, mixed with gunpowder, was used at one time in Prussia for heavy guns, and a black powder containing barium nitrate, sulphur, and charcoal was also used. Wynants, in Belgium, introduced a gunpowder for military purposes, in which nitre was partially or wholly replaced by barium nitrate, the grains being dusted over with gunpowder to increase the inflammability. It was found to be unsuitable for small arms on account of its slow combustion, and for cannon because of its 'fouling,' and was only used as a blasting powder.

Barium nitrate is chiefly used as a constituent in some modern military and sporting smokeless powders, but is occasionally suggested as the oxidising agent in blasting powders, for example, Easton (Eng. Pat. 18551, 1909) proposed a mixture of barium nitrate, trinitrotoluene, and aluminium powder for this purpose; and Burrows (U.S. Pat. 968919, 1910) specifies a mixture of 32 parts barium nitrate, 10 parts of toluene, and 8 parts of aluminium, with or without the addition of charcoal and paraffin wax.

Ammonium Nitrate Mixtures.

Sprengel, in 1873, showed that a mixture of ammonium nitrate and lampblack or charcoal, mixed with ordinary sporting powder, when fired in a rifle, caused a considerable increase in the initial velocity of the bullet, as compared with the velocity imparted by the same weight of sporting powder (Chem. Soc. Proc. 1873, 805). Ammonium nitrate, although containing 60 p.c. oxygen, having a combustible base, has only 20 p.c. oxygen available for the oxidation of other substances: $NH_4NO_3=N_2+2H_2O+O$; whilst potassium nitrate has 39·6 p.c. available oxygen, supposing K_2O to be formed. Ammonium nitrate melts at about 100°, and begins to decompose at 200°, undergoing what is practically an internal combustion. If heated suddenly to a high temperature, as by projecting it on a red-hot surface, it deflagrates violently, and De Bruyn, in 1891, showed that it can be detonated by the use of a sufficiently powerful detonator. The great drawback to the use of ammonium nitrate in explosive mixtures is that it is extremely hygroscopic.

An explosive powder for use in guns and for blasting purposes, patented by Gaens in 1885, and termed *amide powder*, is a mixture of ammonium and potassium nitrates with charcoal. The constituents were used in such proportions as to give, on ignition, potassamide KH_2N, in accordance with the equation:

$$KNO_3+NH_4NO_3+3C=KH_2N+H_2O+CO+2CO_2+2N_2,$$

according to which the powder should be composed of 101 parts by weight potassium nitrate, 80 parts ammonium nitrate, and 40 parts charcoal. The potassamide is stated to be volatile at high temperatures, increasing the useful effect of the explosive, and burning without residue. It is claimed further for the *amide powder* that when burned it leaves very little residue, and gives much less smoke than ordinary gunpowder.

A so-called smokeless powder, known as '*Hebler powder*,' was at one time manufactured in Switzerland, and consisted of a mixture of nitre, ammonium nitrate, sulphur, and charcoal. It was practically non-hygroscopic.

Not only does ammonium nitrate leave no solid residue on combustion, but its use in explosives has been found to greatly reduce the temperature of explosion, and this has caused it to be very largely employed in modern so-called 'safety explosives' for use in fiery mines. Nobel, in 1885, patented the use of ammonium nitrate alone as an explosive, but it has been found that the addition of some combustible substance, not explosive in itself, is necessary to form an efficient blasting agent.

These explosives are used with thoroughly water-proofed wrappers, treated with paraffin, ceresin, and resin, crude vaseline, petroleum products, &c., and the particles of nitrate are frequently coated with similar substances, or with the other constituents of the mixture, from solution or by fusion, so as to render them non-hygroscopic. The addition to ammonium nitrate mixtures of several substances, such as semi-solids made of glue, dextrin, &c., aniline metallic compounds, such as aniline copper sulphate, kieselguhr, &c., has been patented to counteract the action of atmospheric moisture, by absorbing any moisture originally present, or subsequently taken up on storage, and so leaving the explosive constituents in a dry state.

The ammonium nitrate mixtures are non-sensitive to shock, and require a strong detonator to ensure there is not a 'miss-fire,' and to detonate them completely and so develop their full force. Many of these mixtures are extremely difficult to ignite, and almost impossible to keep burning.

Le Chatelier has proposed to crystallise a little potassium chlorate with the ammonium nitrate to render the mixtures more sensitive. Mere addition of the chlorate is inadmissible because of the great danger in mixing, and the action of the mixtures is also somewhat irregular; the salts being isomorphous, they may be crystallised together in any proportions, and these difficulties overcome.

The following are some of the more important ammonium nitrate explosives, containing simple combustible substances:—

Cologne Rottweil contains 93 p.c. ammonium nitrate, 4·9 p.c. vegetable oil, 1·2 p.c. sulphur, and 0·9 p.c. barium nitrate. This explosive is manufactured in this country under the name of *Pembrite*.

Dahmenite at one time consisted of a mixture of the nitrates of potassium and ammonium with naphthalene. *Dahmenite A*, the modern variation, is composed of 91·3 p.c. ammonium nitrate, 6·5 p.c. naphthalene, and 2·2 p.c. potassium dichromate. The naphthalene is melted with the nitrate, so as to coat and waterproof it.

Wetter-dynammon, an Austrian safety explosive, contains 94 p.c. ammonium nitrate, 2 p.c. potassium nitrate, and 4 p.c. charcoal.

Electronite, a 'permitted' safety explosive made by Curtis and Harvey at Tonbridge, is a mixture of 75 p.c. ammonium nitrate, and 5 p.c. barium nitrate with wood meal and starch. The products of detonation are chiefly water, nitrogen, and a little carbon dioxide, and the flame is of too low a temperature to fire explosive gas mixtures.

Electronite No. 2 consists of 95 p.c. of ammonium nitrate and 5 p.c. of wood meal and starch.

Fractorite contains 90 p.c. ammonium nitrate, 4 p.c. resin, 4 p.c. dextrin, and 2 p.c. potassium dichromate.

Progressite contains 89·1 p.c. ammonium nitrate, 4·7 p.c. aniline hydrochloride, 6 p.c. ammonium sulphate, and 0·2 p.c. colouring matter.

Romite, a Swedish explosive invented by Sjöberg (Stockholm, Eng. Pat. 11658, 1887), was a mixture of ammonium nitrate mixed with a solid melted hydrocarbon (naphthalene, paraffin, and the like) gelatinised with a liquid hydrocarbon (such as paraffin oil), and contains pure or similarly gelatinised potassium chlorate. It was found to be unsafe, owing to the interaction between the nitrate and chlorate.

Westfalite is made by the Westphälisch-Anhaltische Sprengstoff-Actien-Gesellschaft. *No.* 1 contains 95 p.c. ammonium nitrate and 5 p.c. of resin or gum-lac. In *No.* 2, 4 p.c. of the ammonium nitrate is replaced by nitre; and in *Westfalite improved*, 3 p.c. of ammonium nitrate is replaced by potassium dichromate. The ingredients are ground together with alcohol or other solvent of the resin, and then heated to drive out the solvent, ground further and compressed into cartridges by a special shaking machine.

The nitro derivatives of the aromatic hydrocarbons, which, as a rule, are not in themselves explosive, form powerful explosives when mixed with ammonium nitrate.

Amvis is a mixture of 90 p.c. ammonium nitrate, 5 p.c. wood meal, and 5 p.c. of chlorodinitrobenzene, or of a mixture of dinitrobenzene and chlorinated naphthalene.

Bellite, invented by Lamb, of Stockholm, is a mixture of ammonium nitrate with metadinitrobenzene. *No.* 1 contains 16·5 p.c., and *No.* 3, 7·5 p.c. of the nitrohydrocarbon.

The mixture is heated to a temperature of between 50° and 100°, in order to coat the particles of the nitrate with the fused nitro compound, and compressed into cartridges before the mixture is cold. In earlier mixtures, other nitrates were used, and the specification mentions other nitrohydrocarbons. Bellite is difficult to ignite, and ceases to burn if the source of heat is removed. It is claimed to be a very powerful and safe explosive for use in fiery mines, and can only be fired by a fulminate detonator.

Faversham powder is a 'permitted' explosive, manufactured by the Cotton Powder Co. It consisted at one time of 85 p.c. ammonium nitrate, 11 p.c. dinitrobenzene, 1·5 p.c. ammonium chloride, and 2·5 p.c. sodium chloride; but more recent compositions are: *No.* 1, 84–86 p.c. ammonium nitrate, 10–12 p.c. trinitrotoluene, 1–2 p.c. ammonium chloride, 1–3 p.c. sodium chloride, and 0–2½ p.c. moisture; and *No.* 2, 87–93 p.c. ammonia nitrate, 9–11 p.c. dinitrotoluene, and 0–1 p.c. moisture. The explosive is contained in a metal case and fired by a No. 6 detonator.

Favier's explosive, *Ammonite* or *Miner's safety explosive*, first patented in 1883 by Favier of Paris, is a mixture of ammonium nitrate, mono-, di-, or trinitronaphthalene, and a little ammonium chloride, mixed and compressed whilst warm into metal cartridges, and coated with a solution of lac or resin. *No.* 1 contains 88 p.c. ammonium nitrate, and 12 p.c. dinitronaphthalene; *No.* 2 contains 90 p.c. of No. 1 with 10 p.c. ammonium chloride.

Verstärktes chromammonit, reinforced chromammonite, is a modern German safety explosive containing 70 p.c. ammonium nitrate, 10 p.c. potassium nitrate, 12·5 p.c. trinitrotoluene, 7 p.c. chrome ammonium alum, and 6·5 p.c. vaseline.

Grisounit is a French safety explosive containing 86–88 p.c. ammonium nitrate, and 14–12 p.c. trinitrotoluene. *Grisounit Favier*, a similar explosive, is composed of 91·5 p.c. ammonium nitrate and 8·5 p.c. dinitronaphthalene.

Negro powder, as authorised for manufacture in this country, is a mixture of 86–90 p.c. ammonium nitrate, 9–11 p.c. trinitrotoluene, 1–3 p.c. graphite, 0–1 p.c. moisture, and a little colouring matter. The cartridges are wrapped in paraffined paper, and are fired by a No. 6 detonator.

Nitroferrite contains 93 p.c. ammonium nitrate, 2 p.c. trinitronaphthalene, 2 p.c. potassium ferricyanide, and 3 p.c. of crystallised sugar.

Roburite, patented by Roth of Charlottenburg, in 1887 (Eng. Pat. 267*a*, 1887), had as a new feature the use of a chlorinated nitrohydrocarbon, chlorinated dinitrobenzene, said to render the explosive more sensitive, and also increase the dynamic effect, but all samples do not now contain this substance. Large quantities are manufactured in England near Wigan. *No.* 1 contains 87·5 p.c. ammonium nitrate, 7 p.c. dinitrobenzene, 5 p.c. ammonium sulphate, and

0·5 p.c. potassium permanganate, and *No.* 3 87 p.c. ammonium nitrate, 11 p.c. dinitrobenzene, and 2 p.c. chloronaphthalene. In later samples, trinitrotoluene is used in place of dinitrobenzene, with wood meal and potassium permanganate. The dried nitrate is incorporated with the molten nitro compound and compressed into cartridges as usual. Roburite has a brownish-yellow colour. It burns readily, but does not explode on burning. It is not sensitive to shock, friction, or pressure; it is practically flameless, and safe in fiery mines. It is more powerful than gunpowder, and its effect is not shattering.

Securite, a safety explosive invented by Schöneweg, in 1886, consists of 74–85 p.c. ammonium nitrate, and 15–26 p.c. metadinitrobenzene. Later varieties, called *Flameless securite*, also contain ammonium oxalate, and sometimes trinitrobenzene and trinitronaphthalene are used. The explosive is made by dissolving the salt in water, evaporating, drying at 80°, and adding the nitrohydrocarbon. The mixtures are coated with nitrated resin.

Withnell powder is a mixture of 88–92 p.c. ammonium nitrate, 4–6 p.c. trinitrotoluene, 4–6 p.c. dried flour, and 0–1·5 p.c. moisture. The explosive is contained in a water-proofed linen-paper wrapper, and fired by a No. 7 detonator.

Thunderite contains 92 p.c. ammonium nitrate, 4 p.c. trinitrotoluene, and 4 p.c. flour.

Titanite No. 1 is a mixture of 85–88 p.c. ammonium nitrate, 6–8 p.c. trinitrotoluene, 4·5–6·5 p.c. charcoal dried at 100°, and 0–1 p.c. moisture.

Steele, in 1906 (Eng. Pat. 4115), proposed a mixture of 85 p.c. ammonium nitrate with 15 p.c. of nitrated resin, or a nitrated mixture of resin and starch; the latter is added in three successive portions, each portion being treated with atomised methylated spirit. The resin in this way is caused to coat the particles of nitrate and render them non-hygroscopic. In some cases 1–5 p.c. powdered aluminium may be added.

Ammonium nitrate mixtures with organic basic substances and their nitrates, such as aniline, guanidine nitrate, and urea nitrate, have been proposed. Kübin (Eng. Pat. 11502, 1894) patented a mixture of 75–95 p.c. ammonium nitrate and 5–25 p.c. aniline or toluidine nitrate. The Carbonite Syndicate, Ltd., in the same year, proposed a mixture of 94 p.c. ammonium nitrate and 6 p.c. aniline hydrochloride, under the name of *Progressite*. Girard (Fr. Pat. 350371, 1904) claims that a powerful explosive is formed by fusing together 80 parts ammonium nitrate and 88 parts guanidine nitrate.

A class of ammonium nitrate safety explosives has come into use, in which a little nitroglycerin, gelatinised with soluble nitrocellulose, is added to overcome the insensitiveness of the mixture, but not containing enough of this constituent to place them amongst the dynamites. Explosives of this type are:

Donarit, which contains 80 p.c. ammonium nitrate, 12 p.c. trinitrotoluene, 4 p.c. flour, 3·8 p.c. nitroglycerin, and 0·2 p.c. collodion cotton.

Ammon-carbonit is composed of 80·3 p.c. ammonium nitrate, 5 p.c. potassium nitrate, 6 p.c. coal-dust, 4·5 p.c. powdered starch, 4 p.c. nitroglycerin, and 0·2 p.c. collodion cotton.

Later forms of *Rexite*, included under dynamites, really come in this class:

Escales, of Munich, in 1899, first proposed the use of aluminium in an explosive, which was manufactured under the name of *Wenghœffer* (Eng. Pat. 24377), whilst in 1900 von Dahmen (Eng. Pat. 16277) claimed the use of aluminium, magnesium, or other light metal mixed with an oxidising agent, a suitable mixture suggested consisting of ammonium nitrate, aluminium, and charcoal in the proportions $4NH_4NO_3+2Al+C$. Subsequently, the charcoal was omitted, and an explosive suggested on the basis of the equation:

$$3NH_4NO_3+2Al=Al_2O_3+6H_2O+3N_2.$$

Von Dahmen's explosive is now on the market under the name of *Ammonal*, and has given very good results, both as a mining explosive and as a high explosive for shells, the proportion of aluminium being varied according to the effect desired. The 'ammonal' permitted in this country as a mining explosive has the composition 93–97 p.c. ammonium nitrate, 4–6 p.c. aluminium, and 0–1 p.c. moisture, the explosive being contained in a thoroughly water-proofed case.

Ammonal B has the composition 94–96 p.c. ammonium nitrate, 2·5–3·5 p.c. aluminium, 2–3 p.c. wood charcoal, and 0–1 p.c. moisture.

Ammonal is very insensitive, and burns with difficulty. It is said to be one of the safest explosives known. It is fired with the usual detonator, and the products of combustion are said to be harmless. The powdered aluminium protects the nitrate from moisture, and the explosive is very stable, being unaffected by variable atmospheric conditions. Shells in Austria-Hungary filled with 'ammonal' have been found in good condition after over 10 years' storage.

Since the introduction of 'ammonal,' aluminium has been added as an ingredient in many other explosives, chiefly in mixtures of the ammonium nitrate class with nitrohydrocarbons. The aluminium is usually used in the form of powder, which is made by first pouring the molten metal into water, and then pounding the small irregular fragments so produced, after drying, under stamp-mills until a sufficiently fine powder is obtained. The use of aluminium and other easily oxidisable metals in the form of 'metal wool,' has been patented, the fineness of division being said to exert a considerable influence on the force of the explosive.

It is claimed that the oxidation of the aluminium sets free a large amount of heat, and that the mechanical effect of the explosives is considerably increased. Bichel, however (Zeitsch. angew. Chem. 1905, [18] 1889), contends that the results showing this increase have been obtained in the lead block test, and are fallacious, and that actual use in mines has demonstrated that the increase in efficiency due to the addition of aluminium, is extremely slight. He affirms that aluminium can only be added economically to those explosives which have a low temperature of explosion; as with others, although there is some increase in the temperature of the explosive, it is more than counterbalanced by the decreased volume of gas produced.

Macnab and the Ammonal Explosives Co., Ltd. (Eng. Pat. 16514, 1904) propose the addition of potassium dichromate to explosives of

the 'ammonal' type. It is claimed that in this way more aluminium may be used, giving greater explosive power, without diminishing the safety of the explosive. A mixture suggested is: 85·5 p.c. ammonium nitrate, 8 p.c. aluminium, 2·5 p.c. charcoal, and 4 p.c. potassium dichromate, or similar mixtures in which a hydrocarbon or nitrohydrocarbon replaces the charcoal.

Besides aluminium and magnesium, many other metals and similar substances which yield oxides reducible with difficulty, including copper, zinc, iron, silicon, ferro-silicon, silicon carbide, various alloys, calcium, boron, and such rare metals as those of the cerium group, have been proposed and patented for addition to explosive mixtures.

The metals may be mixed with other oxidising agents than ammonium nitrate, for instance, barium nitrate has been proposed in recent mixtures with aluminium.

Lead nitrate has been proposed as the oxidising agent in explosive mixtures, together with the usual nitrohydrocarbons, or other explosive or semi-explosive compounds, for example, de Macar (Eng. Pat. 10456, 1900) proposes mixtures containing lead nitrate mixed with 17 p.c. dinitroxylene, 10 p.c. aminoazobenzene, or 45 p.c. dinitrocellulose. Ermel (Fr. Pat. 377509, 1907) claims that the addition of lead nitrate to ammonium nitrate explosives ensures certainty of detonation, the increased sensitiveness being counteracted by the addition of a small proportion of glycerol or liquid hydrocarbon.

Chlorate Mixtures.

The chlorates contain a large store of available oxygen, with which they part at a comparatively low temperature, and with combustible substances yield extremely brusque and violent explosives. Berthelot (Mem. des Poudres et Salpêtre, 1900–1910) has shown that potassium chlorate alone can be made to detonate, by allowing a small drop of the fused salt to fall on a red-hot surface. Chlorate mixtures are readily exploded by friction or percussion, rendering their manufacture highly dangerous, and they are all liable to spontaneous ignition, if the ingredients contain, or are liable to generate, traces of acid. A further drawback to their use is that their sensitiveness to percussion and friction frequently increases on keeping and exposure alternately to moist and dry conditions,—a phenomenon that has been partly attributed to fine crystals of chlorate crystallising out on the surface of the mixture.

Potassium chlorate mixtures. Berthollet, who discovered potassium chlorate in 1788, proposed its use as a substitute for nitre in explosive mixtures, but early experiments led to several serious accidents and temporary abandonment of its use. Since that time innumerable mixtures have been patented, usually with some attempt to counteract the extreme sensitiveness of the mixtures, by the addition of some deadening agent, to coat the grains of chlorate, or some special mechanical expedient, such as only mixing the chlorate and combustible immediately before use.

The usual combustible substances, sulphur, charcoal, peat, tan, sawdust, bran, starch, gum, sugar, and frequently potassium ferrocyanide and realgar, have been proposed, together with such deadeners as tar, pitch, paraffin, ozokerite, soap, glycerol, a syrup of grape sugar, boiled linseed oil, and indiarubber solution. The mixtures were frequently proposed to be used in a moist pasty condition.

Very few need be cited as examples. *Kinetite* was an explosive proposed by Petry, Fallenstein, and Lisch (Eng. Pat. 10986, 1884), consisting of potassium chlorate incorporated with nitrobenzene, thickened and gelatinised with a little collodion cotton and sulphur, as precipitated antimony sulphide. A modified 'kinetite' was made by omitting the antimony pentasulphide. It required a high temperature for ignition, and did not explode on heating. It was, however, very sensitive to friction and percussion, and so chemically unstable that its manufacture in this country was not authorised. Among foreign attempts may be mentioned *Petrofracteur*, favourably reported on by an Austrian military committee, consisting of 67 p.c. potassium chlorate, 20 p.c. potassium nitrate, 10 p.c. nitrobenzene, and 3 p.c. antimony sulphide; and Turpin's explosive, *Duplexite*, a mixture of 70 p.c. potassium chlorate, 10 p.c. charcoal, 10 p.c. dinitrobenzene, and 10 p.c. coal tar (Fr. Pat. 189426, 1888). In England, Kitchen (Eng. Pat. 11102, 1889) submitted a sample of explosive to the Home Office authorities, containing 3 parts potassium chlorate, 7 parts potassium nitrate, 7 parts sugar, and 1 part coal-dust and paraffin oil, that was favourably reported on, but was never put on the market; and practically the only chlorate mixture that was ever used, until some ten years ago, was *Asphaline* (Eng. Pat. 2488, 1881), which consisted of 54 p.c. potassium chlorate, 42 p.c. bran, and 4 p.c. nitre and potassium sulphate. The mixture was deadened with paraffin, ozokerite, or soap, and coloured pink with fuchsine. This explosive was manufactured at Llangollen, but it was not a practical success, owing to its bulky nature, and the licence for manufacture was subsequently withdrawn.

For many years no explosive containing potassium chlorate was licensed, and invention was turned in other directions, owing to the high cost of chlorate explosives, and the greater explosive power of such explosives as dynamite and guncotton. On the introduction of electrolytic potassium chlorate, the price was greatly reduced, and efforts were again made to obtain a practical chlorate explosive. The first electrolytic chlorate factory was started at Villers-sur-Hermes, in Switzerland, in 1889.

Street, in 1897, invented *Cheddite* (Eng. Pat. 9970, 1897), the name being derived from Chedd in Switzerland, where it was first made. This explosive satisfied all tests, and is now very largely used as a blasting explosive. The composition of cheddite is constantly undergoing change in detail, but it is essentially a mixture of potassium chlorate with one or more nitrohydrocarbons and castor oil. Some examples are: *Type* 41, 80 p.c. potassium chlorate, 12 p.c. mononitronaphthalene, and 8 p.c. castor oil. *Type* 60, 80 p.c. potassium chlorate, 12 p.c. mononitronaphthalene, 6 p.c. castor oil, and 2 p.c. picric acid. *Type* 60 *bis*, 80 p.c. potassium chlorate, 13 p.c. mononitronaphthalene,

5 p.c. castor oil, and 2 p.c. dinitrotoluene. A 'cheddite' frequently used in this country has a similar composition to '60 *bis*,' with the proportions of mononitronaphthalene and dinitrotoluene reversed.

Colliery cheddite, as permitted for use in this country, has the composition 76·5–79·5 p.c. potassium chlorate, 14·5–15·5 p.c. mononitronaphthalene, 1·5–2·5 p.c. dinitrotoluene, 4·5–5·5 p.c. castor oil, and 0–1 p.c. moisture.

The method of manufacture of 'cheddites' is to heat the castor oil by steam, in a jacketed enamelled iron pan, to a temperature of 70°. The nitrohydrocarbon, or nitrohydrocarbons, are then added, and when the mass is molten and homogeneous, it is allowed to cool to 55°, when the warm and dry powdered chlorate is mixed in by means of a wooden spatula, and stirred until all white particles have disappeared. 25 kilos. of material can be made in about 7 minutes. Finally, the mixture is poured on to a wooden bench, allowed to cool to about 30°–35°, the mass being still somewhat plastic, and then crushed by rolling it with a wooden roller. The rolling process is repeated when the mass is cold. The finished explosive is in the form of brownish-white grains.

The stability of 'cheddites' is said to be increased on prolonged storage. They are insensitive to shock and friction at ordinary and at very low temperatures, and burn more or less rapidly, without any tendency to explode even when fired in large masses. Keeping for a long period at 120° causes no decomposition. At 200° the oil decomposes, the nitro- compounds volatilise, and the mass dries and blackens; and they do not deflagrate until heated to the temperature of decomposition of the chlorate. 'Type 60' is said to be about as powerful in blast-holes as 'dynamite No. 1,' although it only produces about half the effect of the dynamite in the lead-block test.

Deering, in 1905, found that a 'cheddite,' having the composition 73 p.c. potassium chlorate, 16 p.c. dinitrotoluene, 6 p.c. starch, and 5 p.c. castor oil, gave an explosive effect in a lead block = 0·75, guncotton being unity, and that a thin layer between hardened steel surfaces required a blow of 120 foot-lbs. per sq. inch to cause slight charring in one part, whilst, with a blow of 160 foot-lbs. per sq. inch, the explosive practically all fired.

Many explosives of the Street type have been introduced since 'cheddite,' various nitrohydrocarbons being combined with the chlorate. Improvements have been directed towards minimising the chance of exudation in hot climates. Street himself (Eng. Pat. 12760, 1898) proposed to use a sulphurated oil, fat, or fatty acid, made by heating the oils or fats with sulphur at 180° until they thicken, instead of ordinary oil. Girard (Eng. Pat. 214, 1900) thickened the oil with 10–15 p.c. hard or *soft* soap, and Bonnet (Zeitsch. angew. Chem. 1901, [44] 1120) displaced part or the whole of the oil by the free fatty acids.

Pyrodialite, introduced by Turpin in 1899, is prepared in two forms. First, Nos. 0 and I., explosives with flame, containing respectively 88 and 80 p.c. potassium chlorate, 5 and 6 p.c. vegetable charcoal, 10 and 18 p.c. neutral gas tar, and 3 and 4 p.c. sodium or ammonium dicarbonate. Second, Nos. II. and III., explosives without flame, in which about half the chlorate is replaced by sodium or potassium acetate, the other ingredients being approximately in the above proportions. Later, Turpin proposed the addition of 10–50 p.c. nitroglycerin to render these explosives more sensitive to detonation, and prepared similar explosives with ammonium perchlorate.

Ammonia nitrate powder is an explosive composed of 80 p.c. ammonium nitrate, 5 p.c. potassium chlorate, 10 p.c. nitroglucose, and 5 p.c. coal tar.

In 1908 a chlorate mixture called *Colliery Steelite*, consisting of 74 p.c. potassium chlorate, 25 p.c. so-called nitrated resin, and 1 p.c. castor oil, was licensed as a safety explosive. Steele (Eng. Pat. 22095, 1909) has proposed a safety explosive containing 85–97·5 p.c. potassium chlorate, 2·5–15 p.c. liquid vaseline of sp.gr. 0·885–0·89. *Kohlensilesia* 4.4 is a German safety explosive containing 80 p.c. potassium chlorate, 16 p.c. resin, and 4 p.c. nitrated resin.

The use with chlorate of explosive compounds like nitroglycerin and guncotton has also been patented. Potassium chlorate is a constituent of nearly all detonating compositions, used as initial detonating agents for other explosives.

Other potassium chlorate explosives are mentioned under 'Sprengel Explosives.'

Other chlorates. *Sodium chlorate* is frequently substituted for the potassium salt in the various mixtures mentioned. For example, 'cheddites' are manufactured of the compositions *Type* 41*N*, 80 p.c. sodium chlorate, 12 p.c. nitronaphthalene, and 8 p.c. castor oil; and *Type* 60*N*, 80 p.c. sodium chlorate, 13 p.c. nitronaphthalene, 2 p.c. dinitrotoluene, and 5 p.c. castor oil. These mixtures have very similar properties to those containing potassium chlorate.

Barium chlorate has been proposed in a few mixtures, but its application is practically limited to pyrotechnic compositions.

Ammonium chlorate yields extremely powerful explosive mixtures, but on account of its instability, it has no practical value.

Perchlorate Mixtures.

Perchlorates contain a larger percentage of oxygen, and decompose at higher temperatures than the chlorates. Mixtures containing them are not only more powerful, but also much less sensitive to ignition, percussion, and friction, and consequently are safer to store and use than the corresponding chlorate mixtures. As with chlorates, the electrolytic production of these compounds, cheaply and in a pure state, has led to their largely increased use in recent years.

Potassium and *sodium perchlorate mixtures.*—Formerly, potassium, and occasionally sodium, perchlorate was mainly used, combined with the usual combustible or explosive ingredients, but their use has now been almost entirely superseded by the ammonium salt. However, Trench (Eng. Pat. 8358, 1908) proposed the addition of 5–20 parts of potassium perchlorate to 100 parts of gunpowder to increase the strength and regularity of the explosive, and in the same year, Harris (Eng. Pat. 28012, 1908) suggests mining explosives, consisting of mixtures of potassium perchlorate and carbon with

naphthalene and benzene, and other nitro derivatives in various proportions. Small proportions of paraffin oil and castor oil are also added.

Ammonium perchlorate mixtures. In 1898 Alvisi (Rev. prod. chim. 2, [6] 83, and Eng. Pat. 25838, 1898) proposed the use of ammonium perchlorate, then made from the sodium salt by double decomposition with ammonium nitrate, in explosive mixtures. He claimed that it increased the explosive and propulsive force of the mixture, as well as the ratio of the former to the latter. The ammonium perchlorate was substituted for the other oxidising salts in the proportion of their available oxygen, and sulphur or a metallic sulphide was added to counteract the insensitiveness to ignition or detonation, and he pointed out that the maximum effect of the mixtures is preferably obtained by the use of detonators themselves containing ammonium perchlorate.

Besides having a large percentage of available oxygen, ammonium perchlorate evolves a large amount of gas and heat on decomposition. The decomposition is rapid and the velocity of the explosion wave is great.

It is non-hygroscopic and insensitive when pure; but the insensitiveness of the salt is greatly diminished if it contains even small quantities of ammonium chlorate. Alvisi, later (Gazz. chim. ital. 31, i. 221), confirmed experimentally, by testing various mixtures with combustible and explosive substances, the theoretical advantages of ammonium perchlorate over all other oxidising salts, except ammonium chlorate; and Carbonelli (L'Ind. chim. 1910, 209) obtained equally favourable results.

Explosives containing ammonium perchlorate have the disadvantage of generating hydrochloric acid, and occasionally chlorine in the mine. This drawback is usually overcome by the addition of potassium or sodium nitrate, but manganese or its compounds, oxides, silicide, boride, manganate, or permanganate, have also been suggested for the same purpose.

Ammonium perchlorate is now used in combination with the various combustible and explosive substances mentioned under the other oxidising salts. Yonck (Eng. Pat. 24511, 1903) suggested a series of safety mining explosives containing ammonium perchlorate, amongst which are: (1) 21·2 p.c. ammonium perchlorate, 37·3 p.c. sodium nitrate, and 11·5 p.c. naphthalene; (2) 37·4 p.c. ammonium perchlorate, 27·17 p.c. sodium nitrate, 8·34 p.c. ammonium nitrate, and 27·09 p.c. trinitronaphthalene; and (3) 48·4 p.c. ammonium perchlorate, 33·8 p.c. calcium oxalate, and 17·8 p.c. trinitrotoluene. Webster (Eng. Pat. 18622, 1909) proposed a mixture of 35 p.c. ammonium perchlorate, 45 p.c. sodium nitrate, 10 p.c. dinitrobenzene, and 10 p.c. sawdust, or the same mixture with 2 p.c. of the sawdust replaced by vaseline.

Some 'cheddites,' containing ammonium perchlorate are: 'Type B,' 82 p.c. ammonium perchlorate, 13 p.c. dinitrotoluene, and 5 p.c. castor oil; and 'Type C,' 50 p.c. ammonium perchlorate, 30 p.c. sodium nitrate, 15 p.c. dinitrotoluene, and 5 p.c. castor oil.

Metals are used in mixtures suggested by Bowen (Eng. Pat. 21481, 1903) as a shell powder, 75 p.c. ammonium perchlorate, 12 p.c. aluminium, and 13 p.c. paraffin, and as a blasting powder, 72 p.c. ammonium perchlorate, 11 p.c. aluminium, and 17 p.c. nitronaphthalene; and by Palmer (Fr. Pat. 394833, 1908), in a mining powder, claimed to be non-hygroscopic, stable, powerful, and rapid, consisting of 50 p.c. ammonium perchlorate, 14 p.c. dinitrotoluene, 31 p.c. sodium or potassium nitrate, 5 p.c. aluminium powder, and 5 p.c. paraffin wax.

Mixtures of ammonium perchlorate with explosive compounds have also been proposed; for example, Trench (Eng. Pat. 8358, 1908) proposed to increase the strength and regularity of gunpowder by the addition of from 5 to 20 p.c. of ammonium perchlorate. Explosives compounded of ammonium perchlorate and nitroglycerin, with or without the addition of collodion cotton, and a detonating mixture with mercury fulminate, were suggested by Alvisi (Eng. Pat. 25838, 1898); and Luciani suggests the addition of guncotton to ammonium perchlorate mixtures, more especially with metals (Fr. Pat. 326037, 1902).

Carbonelli (*l.c.*), however, states that ammonium perchlorate tends to dissociate on storage, slowly even when pure, and rapidly in the presence of acid substances, even fatty acids. For this reason he states that the only safe way of using ammonium perchlorate is in explosives of the Sprengel type, where the combustible substance is added immediately before use. He also states that by mixing with 18 p.c. of manganese dioxide, ammonium perchlorate is rendered perfectly stable, the density increased, and evolution of hydrochloric acid on explosion prevented, and suggests turpentine, anthracene oil, or petroleum as the most suitable combustibles.

Other Oxidising Agents.

The permanganates of potassium and sodium, the dichromates of potassium and ammonium, and the peroxides of lead and manganese are all good oxidising substances, and are used to some extent in explosive mixtures, but usually in combination with the other salts, and need no separate mention. The utilisation of the expansive force of liquid air as an explosive has been described by Wood (Eng. Pat. 25025, 1902), and, more recently, liquid air and liquid oxygen have been suggested as the oxygen vehicle in explosives of the Sprengel type.

Sprengel Explosives.

Sprengel (Eng. Pat. 921 and 2642, 1871; Chem. Soc. Trans. 1873, 796) suggested the use, for blasting purposes, of a new class of explosives consisting of mixtures, made immediately before use, of an oxidising agent and combustible substance, in themselves non-explosive.

Some of these explosives are very powerful when detonated by means of mercury fulminate, and they have the advantage of being perfectly safe during storage and transport; but, seeing that they are really manufactured when the mixing takes place, their use in most countries would be forbidden, as this manufacture can only be authorised in a duly licensed factory. Further, they are difficult for a miner to manipulate with cleanliness and safety. In some modern Russian Sprengel explosives, the liquid combustible is contained in a vessel divided into

separate compartments, so that separate portions of the cartridge are uniformly impregnated with separate portions of the liquid, with the result that the explosive action is more uniform.

Sprengel proposed mixtures of nitric acid of about 1·5 sp.gr. with nitrobenzene, naphthalene, nitronaphthalene, and picric acid, and of porous cakes of potassium chlorate with such combustible liquids as carbon disulphide, nitrobenzene, petroleum, and benzene, the mixtures being made in the proportions required for complete combustion.

Rackarock, as used in the United States in 1885 for blasting the Hellgate rocks at the entrance of New York Harbour, was a mixture of 79 p.c. powdered potassium chlorate, and 21 p.c. nitrobenzene. These proportions were found by Abbot to give the maximum effect under water, the intensity of action being 108 p.c. of that of dynamite No. 1. '*Rackarock Special*' contains, in addition, from 12 to 16 p.c. of picric acid.

Rackarock has also been used in other important engineering work, in blasting the headings of the Vosburg Tunnel in Pennsylvania, and in works connected with the first Chinese railways.

Hellhoffite, introduced by Hellhoff of Berlin, was a mixture of dinitrobenzene and nitric acid. It was tried in shells; the two substances mixing during their flight or on impact. Suitably detonated, the mixture is a powerful explosive, more so than guncotton or ordinary dynamite.

Panclastite.—Turpin, under this name (Eng. Pat. 4544, 1881; and 1461, 1882), proposed the use of liquid nitrogen peroxide, a mixture of equal parts of carbon disulphide and nitrogen tetroxide, that is, $3CS_2+5NO_2$, being recommended as giving the maximum effect. The advantages of nitrogen tetroxide over nitric acid are its higher percentage of available oxygen, lower heat of formation, and absence of water, but the disadvantages in its use are obvious.

Oxonite, invented by Punshon (Eng. Pat. 2428, 1883), was a mixture of 46 p.c. picric acid and 54 p.c. nitric acid, sp.gr. 1·5, the acid being contained in the cartridge in a glass tube, which was broken just previously to use.

Donar is a Sprengel explosive invented by Fiedler (Eng. Pat. 8101 and 23284, 1901). The cartridge contains a compressed dry powdered mixture of potassium chlorate and potassium permanganate, with or without potassium dichromate, and a vessel containing a mixture of turpentine with nitrobenzene or phenol; the dry powder being saturated with the fluid shortly before use.

The Soc. Franç. des Poudres de Sûreté (Fr. Pat. 351289, 1905) proposes three combustible mixtures: (1) 27 p.c. orthonitrotoluene, 9 p.c. mononitronaphthalene, and 64 p.c. dinitronaphthalene; (2) 35 p.c. paraffin wax, 50 p.c. orthonitrotoluene, and 15 p.c. trinitrotoluene; (3) 23 p.c. paraffin wax, 13 p.c. nitrotoluene, 13 p.c. trinitrotoluene, and 51 p.c. iron filings. These combustible mixtures are liquefied by warming to about 65°, and mixed with the oxygen-yielding constituents, when required for use. A mixture of nitrates of ammonium, potassium, and aniline is used with (1), potassium chlorate with (2) and (3). Winand (Eng. Pat. 26261, 1907) has patented a mixture of tetranitromethane $C(NO_2)_4$, a liquid boiling at 126°, with petroleum and other carbonaceous matter. Tetranitromethane is a stable substance and only feebly explosive, but somewhat readily exploded by percussion. It dissolves paraffin and other hydrocarbons, forming a pasty mass. It contains 65 p.c. of available oxygen, and is exothermic. '*Oxyliquit*,' introduced by Sieder, (Zeitsch. ges. Schiess-u.-Sprengstoffwesen, 1906, 87) is a mixture of a combustible, usually wood charcoal, with liquid air, or, more recently, liquid oxygen. The explosive is said to act well, but the rapid evaporation of the liquid air is a difficulty, and Fürstenhoff (Fr. Pat. 377103, 1907) proposes safety explosives consisting of a powder of one or more metals, such as aluminium or magnesium, mixed with liquid air or liquid oxygen. The metallic powder, mixed with a quantity of mixed hydroxides of calcium and sodium, which increase the rapidity of the explosive, is fitted into a cartridge, which is then placed in the bore hole, and the necessary quantity of liquid air or oxygen added, and detonation as usual effected by means of fulminate.

Explosive Compounds.

In explosive compounds the combustibles, carbon and hydrogen, exist in infinitely close contact with oxygen in the same molecule. The most important compounds contain nitrogen in loose combination with all or part of the oxygen, so that the chemical equilibrium is more or less unstable. With the requisite exciting force the molecule undergoes more or less complete internal combustion, with almost instantaneous evolution of highly heated gaseous products. Explosive compounds are consequently, as a class, more sudden and violent in their action than the explosive mixtures, and it is evident that the nature of their explosion cannot be graded, as in these mixtures, by varying the ratio of combustible to oxygen.

The most important explosive compounds are produced by the nitration of organic compounds. They may be subdivided chemically into two main groups, the nitro derivatives and the true nitric esters, although technically they are all termed nitro explosives. Besides these two main groups, there are other classes of explosive compounds, such as the fulminates, amino, nitroamino, azo- derivatives, &c.

Nitro Derivatives.

The nitro derivatives are, as a class, more stable and less energetic than the nitric esters. They are, unlike the nitric esters, not liable to spontaneous decomposition if slightly impure, and are stable even in the presence of relatively large quantities of acid. The difference in the explosive characteristics of the two classes is due to a lower percentage of oxygen, and consequent less complete combustion, and a more stable internal structure of the molecule in the nitro derivatives.

They are extremely difficult to explode by simple heating, although Berthelot has shown that even nitrobenzene may be exploded if a small quantity be dropped on to a highly heated surface, but they can all be exploded by the use of a sufficiently powerful detonator. Some of the higher derivatives, such as trinitrotoluene and trinitrophenol, are amongst the most

powerful and important 'high' explosives known, but the lower derivatives are mostly used as constituents of explosive mixtures, principally with ammonium nitrate, potassium chlorate, or ammonium perchlorate, the nitrohydrocarbons being usually fused before mixing with the oxidising ingredient.

Nitrohydrocarbons.

The *nitrobenzenes* are not used as explosives alone, although they can be exploded with difficulty, but the mono- and di- derivatives are used, in combination with oxidising salts or with more explosive compounds, in many modern explosives mostly used for blasting purposes. Numerous instances of these are given. Dinitrobenzene is also used to some extent in some sporting semi-smokeless powders. Tri- and tetra-nitrobenzenes, obtained by the drastic treatment of benzene with mixed acids, are both more easily exploded than the di-derivatives, but little use has been made of them up to the present, although trinitrobenzene has been proposed as a substitute for picric acid as a high explosive by the Chemische Fabrik Griesheim (Ger. Pat. 79477, 1893).

Mono- and dinitro- benzene are active poisons, and care is necessary in handling bare explosives containing them as ingredients.

Nitrotoluenes.

The mono-, di-, and tri-nitrotoluenes are all, but principally the two latter, used as constituents of explosive mixtures, but the trinitro derivative has also become of importance as a high explosive for military purposes.

Trinitrotoluene is also known in different countries under the names 'tolite,' 'trilit,' 'trotyl,' and 'trinol.'

Manufacture.—It is manufactured by the nitration in stages of the carefully purified hydrocarbon, the reaction with the mixed acids being carried out in enamelled iron vessels, and the subsequent washing in centrifugals. The nitration is usually effected by one of two methods. In the first, the toluene is converted into crude mononitrotoluene, by nitrating 1 part of toluene with 3 parts by weight of mixed acids, 2 parts nitric acid, of sp.gr. 1·495, to 3 parts sulphuric acid of sp.gr. 1·84. The mixed mono- derivatives are then converted into dinitrotoluene by the action of twice its weight of the same acid mixture, and finally the product of this second nitration is treated with still stronger acids. A better method, according to Haussermann, is to slowly run with constant stirring 2¼ parts by weight of the mixed acids, 1 part nitric acid to 2 parts sulphuric acid of the strength given above, into 1 part of paranitrotoluene heated to about 60°. The mixture is heated for half an hour at 80°, and then allowed to cool. The crystalline mass of mixed dinitrotoluenes so obtained is dissolved, by the aid of gentle heat, in 4 times its weight of sulphuric acid of the same strength, and then mixed with 1½ times its weight of nitric acid of the same strength, kept cool. The mixture is then heated at 90°–95° with stirring, for about 4 or 5 hours. After cooling, the crude trinitrotoluene is separated from the acid, and washed first with hot water, then with very dilute soda solution, and allowed to solidify. Two qualities of trinitrotoluene are obtained, according to the purity of the materials and the character of the nitration, one having a melting-point between 72° and 74°, the other between 77° and 79°. For military purposes a third quality, having a melting-point between 80·5° and 81·5°, consisting almost entirely of the symmetrical isomeride, is obtained by recrystallisation from alcohol, light petroleum, or toluene. The crystals are freed from residual solvents by whirling in centrifugals, and then heating in an inclined cylinder heated by a hot-water jacket.

Properties.—Trinitrotoluene crystallises from alcohol in sulphur-yellow needles, but when petroleum or toluene is used the crystals are darker and of a light buff colour. Its colour is darkened by exposure to light. When pure, it is without odour and practically insoluble in cold water. It is soluble to a slight extent in hot water, and dissolves readily in alcohol, light petroleum, benzene, and other organic solvents.

Crystals of trinitrotoluene have a density of 1·5, that of the solidified mass after fusion being 1·6.

On application of a flame, trinitrotoluene burns with a very smoky flame. It cannot be exploded by flame, and only quite locally by very strong percussion, but can be readily detonated by means of mercury fulminate. As much as 1000 kilos. have burned away quite quietly in a conflagration, and a rifle bullet may be fired through a solid mass without causing explosion. It may be detonated in the powdered form by means of a No. 3 detonator containing 0·54 gram fulminate composition. A dense black smoke is produced when it is detonated in the open. It is quite safe to handle, and is stable under very varying atmospheric conditions.

Over picric acid it has the distinct advantages that it does not combine with metals, and, generally, has no acid properties. Its dust and vapour are not irritating or injurious to those working with it. It is slightly less powerful than picric acid, but this is an advantage, since in the fragmentation of a shell the pieces are sufficiently large to have considerable destructive effect. The lower bursting effect of trinitrotoluene, as compared with picric acid, is attributed by Kast to its lower density and lower rate of detonation (6700 metres per second against 7100 metres per second). It is a less powerful explosive than wet guncotton, but its effect at a distance is greater.

Shells are usually filled with trinitrotoluene, as with picric acid, by melting the compound and allowing it to solidify in the shells. Bichel (Fr. Pat. 357925, 1905) proposes to use compressed trinitrotoluene, which he had previously shown to have a higher velocity of detonation than in the loose condition, as an explosive for shells, mines, and torpedoes, by cementing together blocks of the compressed material by means of the fused compound, and, in a later patent (Fr. Pat. 369371, 1906), proposes to obtain a higher density than by simple casting, with trinitrotoluene as well as with other fusible nitro-explosives, by casting in a closed vessel, first placed under evacuation, to remove all air bubbles, and then submitting the molten mass, whilst rapidly cooled by means of a water-jacket,

to compressed air or carbonic acid. A density as high as 1·69 has been obtained in this way.

Nobel (Ger. Pat. 212169, 1907) has patented a method of increasing the density of trinitrotoluene, and other suitable nitrohydrocarbons, by first cooling the shell to 0° before pouring in the liquid. Rudeloff, by compression under 3000 atmospheres, has obtained a mass with a density of 1·7, that can be cut and worked like wet guncotton. The detonation of the densified solid is facilitated by using some of the loose trinitrotoluene as a primer.

Trinitrotoluene is also used in considerable quantities for detonators. It is employed either alone, with a priming of mercury fulminate, or as an ingredient in cap and detonating compositions. It is, for example, stated that in a No. 7 detonator the 1·5 grams of fulminate can be advantageously replaced by a mixture of 0·7 gram of trinitrotoluene and 0·5 gram of fulminate.

Trinitrotoluene has been suggested in various mixtures as a high explosive for shells and torpedoes. Bichel (Fr. Pat. 369661, 1906) makes a plastic explosive called '*plastrotyl*,' by mixing it with a solid or liquid resin, such as copaiba balsam, or larch turpentine, with or without the addition of dinitrotoluene and collodion cotton. Rudeloff and Allendorff (Ger. Pat. 201306, 1906) make '*triplastit*,' with a density as high as 2·5 by mixing with a jelly prepared from dinitrotoluene and soluble dinitrocellulose, heating slowly to about 80°, and incorporating, as an oxygen carrier, a mixture of potassium chlorate and lead nitrate.

Trinitrotoluene is a constituent of many modern ammonium nitrate safety explosives.

Other nitrohydrocarbons. The nitrohydrocarbons, largely di- and trinitro derivatives of mesitylene and pseudocumene, obtained by nitrating solvent naphtha, have been proposed by Shulz and Gehre (Eng. Pat. 5687, 1905, and 19565, 1907) for use in explosive mixtures of the usual type, known as '*Vigorite*' and '*Bavarite*.'

The nitronaphthalenes, usually dinitronaphthalene, are occasionally used, principally associated with ammonium nitrate in safety explosive mixtures.

The nitrohydrocarbons of the fatty series have so far met with only a limited use. The Soc. Anonyme d'Explosifs et de Prod. Chim. (Fr. Pat. 394992, 1907) claim the use in particular of mononitromethane, a liquid boiling at about 99°–100°, in smokeless powders with nitrocellulose, or nitrocellulose and nitroglycerin, and the use of tetranitromethane by Winand has already been mentioned under 'Sprengel Explosives.'

Nitrophenols.

The potassium salt of mononitrophenol can be detonated by percussion, and it has been proposed in America (U.S. Pat. 792716, 1905, and 940586, 1909) to use dinitrophenol mixed with picric acid, to lower the melting-point of the latter, and as an ingredient in explosive mixtures, but the only nitro derivative of ordinary phenol used to any extent is picric acid, symmetrical trinitrophenol, which is largely used by itself as a high explosive, and to a limited extent in explosive mixtures, usually of the detonating class.

Picric acid. *Manufacture.*—Direct nitration of phenol with strong nitric acid gives picric acid, but the action is very violent, and there is considerable loss by oxidation, and it is preferable, therefore, to sulphonate the phenol before nitration. The usual process is to mix together equal weights of crystallised phenol and concentrated sulphuric acid in an iron vessel, the mixture being heated to between 100° and 120° by means of superheated-steam coils. The mass is kept stirred until it is completely soluble in cold water, when it is allowed to cool, and twice its weight of water added. The solution is then run gradually into three parts by weight of nitric acid, sp.gr. 1·4, contained in earthenware tanks standing in running water. When the reaction, which is at first very violent, moderates, the vessels are heated by steam until the nitration is complete. The reactions are:

(1) $C_6H_5OH+H_2SO_4=C_6H_4(SO_3H)OH+H_2O$.

(2) $C_6H_4(SO_3H)OH+3HNO_3=C_6H_2(NO_2)_3OH+H_2SO_4+2H_2O$.

The nitrous fumes evolved are condensed and reconverted into nitric acid.

The crystals of picric acid, which separate on cooling, are separated from the mother liquor, and afterwards washed with warm water in a centrifugal machine. The crystals are further purified by recrystallisation from boiling water, centrifugation, and drying on earthenware trays in a steam box at about 35°–38°.

To obtain more perfect purification from the last traces of mineral acids, picric acid is usually converted into its sodium salt by dissolving in hot solution of sodium carbonate. On cooling, almost chemically pure sodium picrate crystallises out; this is centrifugated, washed with cold water, dissolved again in hot water, and the acid precipitated by adding an excess of hydrochloric acid. This is finally purified by washing and centrifugation, and the last traces of acid are volatilised on drying.

Gutensohn (Eng. Pat. 16628, 1900) proposes to add the phenol, dissolved in paraffin or similar oil, directly to the nitric acid, covered with a layer of the same oil, in order to moderate the nitration reaction without sulphonation.

Wenghöffer Ger. Pat. 125096, 1900) suggests aniline as the primary material instead of phenol, as being less subject to variation in market price. It is converted, through sulphanilic acid, into diazobenzene sulphonic acid, which readily yields picric acid on nitration, a yield of 90 p.c. of the theoretical being claimed.

Properties.—Picric acid crystallises in bright pale-yellow plates or prisms. It is sparingly soluble in cold, but more soluble in hot water. It has an exceedingly bitter taste, and its taste and colour are imparted to very dilute aqueous solutions. It is readily soluble in alcohol, acetone, ether, and benzene. It melts at 122·5° to a yellow liquid, and by careful heating may be sublimed without decomposition, the vapours being very bitter and irritating. Suddenly heated, it deflagrates sharply, with a bright-red sooty flame, and Berthelot has shown that a small quantity dropped on a red-hot surface decomposes with explosive violence.

Large masses of picric acid can be heated in

a confined space without explosion, but Berthelot is of the opinion that the explosion of a small quantity by a heated surface may, under certain conditions, cause detonation of a large mass of picric acid.

It is difficult to explode picric acid by direct percussion, but it can be readily detonated by mercury fulminate; 1·5 grams of fulminate act well for the dry powder; even wet picric acid, containing as much as 15 p.c. of water, can be so detonated if a priming of the dry acid is used.

The heat of formation of picric acid is 49·1 cals., and the heat of total combustion in oxygen 618·4 cals. (Berthelot).

Picric acid does not contain sufficient oxygen for complete combustion, and it is 3·49 p.c. deficient for the formation of carbon monoxide, and 45·41 p.c. deficient for the formation of carbon dioxide. Nevertheless, when efficiently detonated, it is one of the most powerful explosives known, exceeding dynamite and compressed guncotton in power, especially when densified by fusion and solidification. The density after casting is 1·6–1·7, and it can be obtained with a still higher density by Bichel's method of casting under pressure.

Sprengel (Chem. Soc. Trans. 1873, 803) was the first to call attention to the explosive possibilities of picric acid in itself, but it was not till 1886 that Turpin made a practical high explosive of it, by suggesting the use of compressed or molten picric acid as a charge for shells. The value of picric acid as a high explosive lies in the fact, as Turpin pointed out, that in this class of explosives the maximum effect does not coincide with complete combustion, but occurs where the carbon is burnt to carbonic oxide, the greater gas evolution more than counterbalancing the smaller heat of combustion. Turpin's first '*Melinite*,' adopted in France as a high explosive for shells, was picric acid made into a colloidal state and densified by the addition of a solution of 3–5 p.c. collodion cotton in alcohol and ether, but very soon this was abandoned in favour of the fused picric acid alone, as Turpin showed this to be still more powerful, and so insensitive that it could only be detonated under strong confinement. The English '*Lyddite*' is simply fused picric acid, melted in large cans, in a carefully regulated hot-air stove, at 130°–140°, and filled directly into the shells, a central cavity being left for the exploder. Picric acid has been used for similar purposes, also for mines and torpedoes, by most other countries under various names, such as 'Ecrasite,' 'Shimose,' 'Pertite,' 'Picrinit,' &c.; in some cases additions of other substances, such as nitronaphthalene, di- and trinitrotoluene, trinitrocresol, being made in order to reduce the melting-point. As the melting-point of picric acid is so high, and its sensibility to percussion increases with the temperature, its fusion on the large scale is to some extent dangerous. Girard (Eng. Pat. 6045, 1905) gives a long list of the melting-points of equimolecular mixtures of picric acid with other nitro derivatives; in all cases the melting-point of the mixture is well below that of the constituent of lower melting-point.

The cast picric acid, when unconfined, is much more difficult of detonation by mercury fulminate than the loose acid; 3 grams of fulminate fired in the mass will not explode it. It may be detonated by using a priming of the loose acid or of guncotton, but much more perfectly by a primer of 'picric powder,' or trinitrotoluene.

On the assumption that the explosion of 'lyddite' is represented by the equation:

$$2C_6H_2(NO_2)_3OH = 3CO_2 + 8CO + C + 3H_2 + 3N_2,$$

de la Roque (Rev. de Chim. Industrielle, 11, 5) has calculated the following constants:—

Heat evolved at constant pressure per kgm.	853·4 kgm.-cals.
Heat evolved at constant volume per kgm.	876·0 „ „
'Potential' (*i.e.* maximum work by unit weight, assuming complete gasification and adiabatic expansion)	272,280 kgm.-metres
Volume of gas from 1 kgm.	683,453 cc. at N.P.T.
Temperature of explosion	2832°
Pressure developed by the explosion of 1 gram in unit volume	8086 kgms. per sq. cm.

Actual analysis has shown that, when explosion takes place, the decomposition is more complicated than this, the products being: carbon monoxide, carbon dioxide, nitrogen, nitric oxide, water, hydrocyanic acid, and residual carbon.

Picric acid is safe to manufacture and transport. The advantages of cast picric acid as a high explosive are many, its physical and chemical stability are very great, and it can be kept for an indefinite period under varying atmospheric conditions; it is difficult to ignite, and it is very insensitive to percussion; is quite safe from the danger of being fired by the shock of the discharge of guns of large calibre, yet when perfectly detonated it is extremely powerful in its bursting effects. On the other hand, there are such disadvantages as its high melting-point, the objectionable nature of its vapours, which not only dye the hair, skin, and clothing of those working with it, but are also extremely irritating, if not harmful. It is difficult to detonate completely, and incomplete detonation yields very deleterious gases. The most serious objection of all, however, is its acidic character, which leads to the formation, in contact with metals and some of their compounds, of picrates, many of which are highly sensitive, the picrates of lead particularly so. Serious accidents have resulted in the use of picric acid, which have been attributed to the formation of these compounds, and for this reason the interiors of the shells are varnished, and lead compounds are carefully guarded against in the lutings used on the screw threads on the shell plugs, and in all paints and varnishes connected with picric acid shells. Trinitrotoluene is free from most of these objectionable features, and there seems reason to think it will more or less replace picric acid in its many uses.

Emmensite (Eng. Pat. 370, 1888), the invention of Emmens of the United States, is produced as crystals, said to be different from picric acid, by the action of fuming nitric acid of sp.gr. 1·52 on picric acid. The explosive was favourably reported upon by the U.S. War Dept., and is said to be satisfactory, both as a propellant and as a high explosive.

Picrates. The picrates, formed by the action of the acid on the metals, their oxides, hydroxides, or carbonates, are well-defined, crystalline compounds, which are quite stable under ordinary conditions, but they are all more sensitive to heat, friction, and percussion than the acid itself. This is true, to some extent, even of the alkaline salts, whilst the picrates, normal and basic, of some of the heavy metals, especially lead, are extremely sensitive and violent. They detonate with violence, and their detonation is sufficient to prime an indefinite amount of picric acid. Ammonium picrate is the most insensitive. It has been proposed as a substitute for picric acid for use in shells, as it has no tendency to form dangerous picrates. A very serious explosion of picric acid, near Manchester, in 1887, was caused by melted picric acid flowing on to litharge, detonating with it, and thereby acting as a primer, causing the detonation of all the picric acid present. In connection with this explosion, Deering showed that very rough mixtures of picric acid with litharge, red lead, lead nitrate, strontium nitrate, lime, &c., detonated violently, and were sufficient to prime a large mass of picric acid. Mixtures of picric acid with certain peroxides will fire spontaneously.

Explosive mixtures containing picric acid and *picrates.* Many years before picric acid was used as a high explosive, attempts were made to use it and the picrates in explosive mixtures. It was recognised that picric acid is deficient in oxygen, and, consequently, picric acid and the picrates were proposed to be used mixed with various oxidising agents. However, the insensibility of picric acid is largely due to its deficiency in oxygen, and for this reason the mixtures with oxidising agents are all much more sensitive to heat, percussion, and friction than the acid itself. Mixtures containing picric acid, with either nitrates, chlorates, chromates, or permanganates, are extremely unstable, and liable to undergo spontaneous explosion, owing to the slow displacement of the highly oxidising acids by the picric acid, in the presence of even traces of moisture, and many serious accidents have been caused by such mixtures. Attempts have been made to increase the stability of picric acid mixtures by coating the particles of the acid with an insensitive and protective film; for instance, Roth (Eng. Pat. 173550, 1886) proposed a mixture of picric acid and ammonium nitrate with a fatty drying oil, and Turpin patented various mixtures of picric acid with gum, oils, fats, collodion jelly, &c.; but the picrates are far preferable to the free acid in explosive mixtures.

The picrates of ammonium, potassium, or sodium are those most frequently used in explosive mixtures. In 1869 Designolle made mixtures of potassium picrate and charcoal with nitre, in proportions varying according to their use, for small-arm and cannon powders, and mixtures of potassium picrate and nitre for filling torpedoes and shells. These mixtures were made in much the same way as ordinary gunpowder; they gave very good results, and were in use for some time in the French Navy. 60 grams of the propellant powders were said to give the same result as 350 grams of ordinary gunpowder, and the intensity of action of the disruptive powder was nearly 70 p.c. of that of dynamite No. 1. In the same year, Brugére and Abel, independently, recommended mixtures of ammonium picrate and nitre. Brugére's powder was composed of 54 p.c. of ammonium picrate and 46 p.c. of nitre. It was insensitive to friction or shock, slow burning, nearly smokeless, in small arms quite as powerful as gunpowder, and non-erosive. Abel's mixture, 3 parts of nitre and 2 parts of ammonium picrate, was at first proposed for use in shells, but afterwards adopted in the Service, under the name of *Picric powder*, as an exploder for priming lyddite shells. It is very stable, burns only locally with slight deflagration on application of flame, and requires strong confinement to develop its force, when it is very powerful. At one time it was manufactured and granulated like Designolle's mixtures, but a mixture of 57 p.c. of nitre and 43 p.c. ammonium picrate, dry mixed, was subsequently adopted. It is easier and safer to make in this way, and the product is also more stable, for the wetting in the old method of manufacture caused the formation of a little hygroscopic ammonium nitrate by double decomposition. Its theoretical decomposition is:

$$5C_6H_2(NO_2)_3ONH_4+16KNO_3 = 22CO_2+18N_2+15H_2O+8K_2CO_3.$$

Ammonium picrate, and more rarely, potassium picrate, mixed with the nitrates of barium, potassium, and ammonium, and other ingredients combustible and explosive, has been the subject of innumerable patents for so-called smokeless and safety powders, usually in America, Austria, or France. Detonating mixtures containing picrates and chlorate of potash have been proposed, and picrate of lead has been suggested for the same purpose. The picrate mixtures generally, however, are shunned in this country, owing to their chemical instability and the extreme danger in their storage and use.

Trinitrocresol is manufactured similarly to picric acid, and has very similar chemical and physical properties. It melts at about 107°. It is acidic and forms explosive salts. It has explosive properties similar to picric acid, and has been used, when cast, as a high explosive for shells and torpedoes, alone and mixed with picric acid. It requires priming, and guncotton is generally used for this purpose. In France it is known as '*Cresylite.*' In Austria the name '*Ecrasite*' has been from time to time applied to high explosives of different composition used for charging shells, but apparently always containing trinitrocresol or its ammonium salt. Trinitrocresol has been used alone or mixed with picric acid, and the ammonium salt has been used alone or mixed with nitre. The ammonium salt is a yellow crystalline solid, melting at about 100°. It burns without explosion unless strongly confined, and is insensitive to friction and percussion. It is stemmed into shells with a wooden rod, or compressed into slabs. A guncotton primer is generally used to ensure complete detonation, but it can be exploded with a 2-gram fulminate detonator. A mixture of trinitrocresol and picric acid in molecular proportions, melted together and mixed with an oxidising salt, has been proposed by Girard (U.S. Pat. 895254, 1908).

The *higher nitrophenols* are all more or less explosive and yield explosive salts, but they have, as yet, met with no practical use.

Nitric Esters.

On nitration, the organic alcohols and carbohydrates yield true nitric esters, or organic nitrates, which are explosive compounds. The internal structure and explosive characteristics of the nitric esters are different from those of the nitro derivatives, but, unfortunately, this difference has not been recognised in the technical nomenclature. The products of nitration of all organic substances, that are explosives, are all technically known as nitro explosives.

With reducing agents, the explosive compounds of this class yield more or less the primary substance of the nitration, and not amino compounds, as do the nitro derivatives, and by the prolonged action of caustic alkalis they give the primary substance and an alkaline nitrate, together with other products of secondary reactions. A simple test serves to distinguish the two classes of nitro compounds. When shaken with sulphuric acid, in a Lunge nitrometer, the nitric esters yield their nitrogen as nitric oxide; the true nitro derivatives do not do so.

The nitric esters, generally speaking, are more powerful explosives than the nitro derivatives, but are less stable, more especially in the presence of foreign substances, such as residual traces of the nitration acids.

Nitroglycerins.

Mono-, di-, and tri-nitric esters of glycerin are possible. Liecke, in 1865, stated that he obtained mono- and di-nitroglycerin by nitrating glycerol at 0° in a mixture of 1 volume of nitric acid, sp.gr. 1·4, and 2 volumes of strong sulphuric acid; and later said that when nitric acid of 1·3 sp.gr. is used the mononitrate is obtained, whilst the dinitrate and trinitrate are respectively obtained by using an acid of 1·4 or 1·5 sp.gr.

Henriot claimed to prepare the mono-compound by nitrating glycerol with a dilute nitric acid containing 3 parts of water to 1 of strong acid; and Wohl (Ger. Pat. 58957, 1890) suggested the use of the mono- and di- compounds for reducing the freezing-point of nitroglycerin.

Mikolajczak did considerable work in 1904 on mono- and di-nitroglycerin (Zeitsch. Gluckauf, 1904, 629); and Will made a full investigation of their preparation, properties, and uses in 1908 (Ber. 41, 1107), from which work the following short description is taken.

Dinitroglycerin. Will prepared dinitroglycerin by the following modification of Mikolajczak's method of preparation. 10 parts of glycerol are slowly stirred into 33 parts of nitric acid, sp.gr. 1·5, kept at a temperature of below 0°, and the mixture allowed to stand for several hours at 10°. The mixture is then poured into 10 parts of water and neutralised with powdered marble. On standing, the greater part of the dinitroglycerin separated as an oil, the remainder being extracted by ether.

Will's method of preparation is to slowly run 100 parts of glycerol, with constant agitation, into 500 parts of ice-cold mixed nitric and sulphuric acids, 3 parts H_2SO_4 to 1 part HNO_3, and 9 parts of water to 100 parts mixed acids. The mixture is then poured into 10 parts of water, and the dinitroglycerin allowed to separate. The acid solution is then neutralised, extracted with ether, the ether distilled off, the separated dinitroglycerin washed with a little water, and dried over sulphuric acid.

Dinitroglycerin can also be obtained by dissolving trinitroglycerin in strong sulphuric acid, diluting the solution with water and extracting with ether.

Dinitroglycerin is a colourless or light-yellow oil, which solidifies below −13°, and distils without appreciable decomposition at 146°; sp.gr. 1·47. It is poisonous like trinitroglycerin. It is soluble to the extent of about 8 p.c. in water, and in all proportions in dilute nitric and sulphuric acids. It is also soluble in ether, alcohol, chloroform, acetone, carbon tetrachloride, and petroleum spirit. In strong sulphuric acid, like the trinitrate, it is denitrated, giving first mononitroglycerin, and eventually glycerol. When dry it dissolves and gelatinises nitrocellulose.

Will succeeded in separating dinitroglycerin into two isomerides by taking advantage of the property of one of them to form a crystalline hydrate. Both isomerides, when dry, have explosive properties resembling those of trinitroglycerin, but become non-explosive in moist air through absorption of water.

Mononitroglycerin was obtained by Will, by a process of crystallisation, from the oil extracted with ether from the neutralised and concentrated aqueous mother liquor obtained in the preparation of dinitroglycerin. He obtained two isomerides, both crystalline solids, melting at 54° and 58° respectively, and freely soluble in water.

Nitrodiglycerin. When glycerol is heated for 7–8 hours at 290°–295°, it is largely converted into diglycerin, with a little triglycerin and higher polyglycerins. The diglycerin can be separated by fractionation, and on nitration gives a product almost identical in properties with nitroglycerin. If a mixture of glycerol and a little diglycerin is nitrated, the resulting product, which contains di- and tetra-nitrodiglycerin, has all the properties of nitroglycerin, but remains fluid at −15° to −20° (Will, Zeitsch. angew. Chem. 1906, 889).

Nitroglycerin. Ordinary nitroglycerin is the trinitric ester of glycerol. It was discovered in 1847 by Sobrero. In a letter to Pelouze (Compt. rend. 24, 247), he states that when glycerol is poured, with stirring, into a mixture of 2 vols. of sulphuric acid of 66°Baumé, and 1 vol. of nitric acid of 43°, cooled by a freezing mixture, the glycerol dissolves therein without perceptible reaction, and that on pouring the mixture into water an oily substance, heavier than water, is precipitated.

Sobrero described some of the properties of nitroglycerin, but did not analyse it.

No practical application of importance of the properties of nitroglycerin was made until 1863, when its preparation on a large scale was commenced by Nobel, who started two nitroglycerin factories near Stockholm and near Lauenburg. It was first called 'pyroglycerin,' afterwards 'glonoine oil,' and still later 'Nobel's blasting oil.' Between 1863 and 1865 increasingly

large quantities of nitroglycerin were made and exported; but serious accidents occurred about the year 1866 in different parts of the world whither the nitroglycerin had been exported, and were followed by legislation on the part of several governments, prohibitive of its use. This restrictive legislation was met by Nobel by the introduction of dynamite in 1866–67, the carriage and use of this preparation of nitroglycerin being comparatively safe. Mowbray, before this time, had manufactured large quantities of nitroglycerin in Massachusetts, and it had been transported for use in the mines in the frozen state.

Manufacture.—The following is a short account of the manufacturing processes in general use for the manufacture of nitroglycerin, with special reference to some recent improvements adopted at the Royal Gunpowder Factory, Waltham Abbey (*see* Nathan and Rintoul, J. Soc. Chem. Ind. 1908, 1903). The chemical basis of the processes is essentially that of Sobrero's method of preparation, but the modern manufacturing plant is of entirely different type from that in use in the earlier factories, and the output has enormously increased.

Prime materials.—The *glycerol* used in the manufacture of nitroglycerin is the purest distilled glycerol obtainable, and practically anhydrous. The presence of impurities in the glycerol leads to the formation, on nitration, of bodies, which render the product unstable and liable to spontaneous decomposition. Its sp.gr. must not be less than 1·26, and it must be free from acid, lime, chlorides, and arsenic. It should also be free from fatty acids; in the process of distillation of the glycerol, fatty acids of the same boiling-point are apt to come over, and when nitrated are difficult to remove from the nitroglycerin. The total residue, after careful evaporation of the glycerol, should be less than 0·25 p.c., of which not more than 0·10 p.c. should be inorganic. Even these tests are insufficient to ascertain the suitability of a glycerol for nitration, and the final verdict depends on a practical nitration test on the small scale; 10 grams of the glycerol are poured very slowly into a mixture of 27½ parts of nitric acid of 1·50 sp.gr., and 72½ parts of sulphuric acid of 1·84 sp.gr. kept quite cold during the addition. The nitroglycerin, after separation, and also the waste acids, are allowed to stand some time in long burettes and the separated nitroglycerin ultimately collected and measured. The yield should be at least 200 p.c. by weight of the glycerol, and, further, no flocculent matter should separate out during the nitration.

At the present time, the various supplies of glycerol at Waltham Abbey are carefully blended to ensure uniformity of manufacture, the blending being performed in large iron tanks holding 10 tons. The glycerol is rendered fluid by heating with steam coils run into an elevator, a strong steel cylinder or egg-shaped vessel, and thence forced by compressed air into a tank in the charge house, which is placed above the nitrating house. The charge of glycerol was formerly weighed, but it is now usually measured in the tank by means of a gauge glass. The glycerol must not be too heated, or, because of its reduced specific gravity, the weight of the charge deduced from the volume in the tank will be incorrect; yet, on the other hand, it must be fluid enough to easily run into the nitrating apparatus.

Acids.—To procure a good yield of pure nitroglycerin, the nitric acid should be practically anhydrous. If the nitric acid be too weak, lower nitrates are formed, which dissolve in the acid mixture. To increase the strength of the nitric acid, and to keep this strength up by removing the water liberated in the nitration, it is necessary to mix the nitric acid with strong sulphuric acid. Nitroglycerin is soluble in either acid, but not in a mixture of the two. The strengths of the two acids and their relative proportions have varied from time to time. In all early large-scale manufacture, the mixed acid was similar in strength and proportions to that used by Sobrero, but the mixture is now usually made from acids of the following description.

The *nitric acid*, prepared by the ordinary methods from sodium nitrate and sulphuric acid, or recovered from waste acids by denitrating, must be at least of 1·5 sp.gr. at 15·5°, and must not contain more than a small quantity of nitrous acid; usually not more than 1·5 p.c. is allowed, but sometimes the limit is as low as 0·5 p.c. The nitric acid should be also free from sulphates and chlorine.

Mowbray introduced the method of freeing the nitric acid from nitrous acid by heating it and passing a current of air through it. At Waltham Abbey, the nitric acid is made by the Valentiner process, which gives a product very free from nitrous acid (*v.* NITRIC ACID).

The *sulphuric acid* must be the purest and most highly concentrated obtainable. It must have a sp.gr. of at least 1·842 at 15·5°, and must contain not less than 96 p.c. by weight of the monohydrate. It should be as free from iron and arsenic as possible, as these substances cause reduction of the nitroglycerin.

Mixed acids.—These acids are mixed in the proportion of 3 parts of nitric acid to 5 parts of sulphuric acid, and glycerol is usually used in the proportion of 1–8 parts of the acid mixture, but in some factories the proportion of acid mixture is as low as 7 or 7½ parts. In this acid mixture there is present nearly 6 p.c. of water over that giving acid monohydrate, and within the last few years it has become a common practice to add Nordhausen sulphuric acid in such quantity as to combine with nearly all this excess of water, an increased charge and yield and less waste acid resulting.

Nathan and others have patented (Eng. Pat. 6581, 1906) the nitration of glycerol with a mixture of Nordhausen sulphuric acid and nitric acid, with the object of obtaining a larger yield; but Guttmann (Chem. Zeit. 1905, 939) holds that, beyond a certain point, increase in the concentration of either acid does not improve the yield of nitroglycerin, and, further, is deleterious to the quality of the product.

The Nordhausen acid is stored in iron drums, and, like the other acids, is first transferred to a steel acid elevator or 'egg,' as it is termed, and thence forced by compressed air into the mixing tank. The large cylindrical steel mixing tanks hold about 60 tons of mixed acid. Nitric acid is run into the tank through a pipe extending to the bottom of the tank, and then the sulphuric

acid added through a pipe in the cover, and the two mixed by compressed air, the fumes evolved pass through a fume pipe into condensing towers. Two tanks are used at Waltham Abbey, so that the mixed acid can be allowed to stand some days before use, in order to allow lead sulphate and other impurities to settle out, and also so that it may be analysed, and any necessary adjustment of composition made. The mixed acid is run from the tanks as required into an elevator, and forced into a cylindrical steel vessel in the charge house to a fixed level determining the charge.

Nitration.—Mowbray carried out the nitration of glycerol in earthenware pots, using a large number of them and small charges. Each pot contained about 17 lbs. of mixed acids, into which 2 lbs. of glycerol was allowed to drop by means of a siphon; the operation of nitration taking place simultaneously in all the vessels. He introduced an important improvement on the old mechanical stirrers, by using compressed air for mixing the glycerol and acids. In later factories large lead vessels with conical covers were used for the nitration, and agitation was effected by the combined use of compressed air and a stirring paddle or helix; the water working the latter being also used for cooling the mixture by passing through lead coils. The glycerol was allowed to fall on a disc fixed to the shaft of the paddles above the level of the acids, from which it was thrown in fine drops on to the surface of the acids. A process of nitration evolving new principles was introduced at Vonges in 1872 by Boutmy and Faucher, and subsequently worked on a large scale at Pembrey in South Wales. They separately mixed the glycerol with part of the sulphuric acid, forming sulphoglyceric acid, and the nitric acid with the remainder of the sulphuric acid. Each of these operations involves the liberation of heat, so that, when these cooled mixtures were themselves mixed, less heat was developed in the actual process of nitration. However, the nitration process takes some 24 hours for completion, and the danger of leaving the nitroglycerin for so long a time in contact with the mixed acids more than counterbalances any advantage derived from the smaller development of heat. Serious explosions took place in various factories using this process, and it is no longer used.

In most modern factories the nitrating apparatus (there are usually two in the building) is a large lead cylindrical tank with a convex or inclined bottom, standing in a wooden vat. Inside the former are lead cooling worms, through which cold water circulates, as well as between the tank and its wooden case. This water is, in many factories, artificially cooled by a refrigerating plant to 10° or less. The agitation is now usually performed in this country with compressed air only, at a pressure of about 20 lbs. per square inch, which is forced through pipes which are led down to and round the bottom of the tank. The tank is closed with a dome-shaped cover of lead, provided with a number of glass inspection windows, through which the various pipes for air, water, and glycerol pass. A glass tube to allow the colour of the fumes to be seen, which is connected with a pipe to carry away the fumes, and a thermometer, also pass through the cover. The mixed acids are run in, from the tank in the charge-house above, and cooled to a temperature of about 16°. The glycerol is then introduced in a spray at the bottom of the tank, compressed air and a simple injection apparatus being used to produce the spray, the contents being kept in a constant state of agitation and well cooled. The rate of flow of the glycerol is regulated so as to keep the temperature of the charge below 22°–25°. If red fumes are noticed at any time in the fume pipe, the inflow of glycerol is cut off, and additional air blown through till the fumes cease. If the evolution of red fumes cannot be stopped, or if the temperature should rise above 30°, and not fall with the full air current on, serious local decomposition is indicated and the charge is at once drowned.

Two pipes, provided with earthenware cocks, leave the nitrating tank at its lowest point, both of which can be opened, in case of danger, and the contents of the tank quickly discharged into the drowning tank—a large wooden tank filled with cold water situated immediately below the nitrating tank, the contents of which can be agitated by means of compressed air.

The whole process of nitration, including the subsequent cooling down, takes about one hour.

In the nitration of glycerol some sulphoglyceric acid is formed, the amount increasing with the quantity of sulphuric acid in the mixed acids. When the waste acids are allowed to stand, the nitric acid partly decomposes this sulphoglyceric acid, and nitroglycerin separates out.

Separation.—In early factories the separation of the nitroglycerin was effected by slowly running the nitrated charge into a large bulk of water contained in lead-lined vats, kept in a state of agitation. The bottom of the tank was inclined and led to a tap through which the nitroglycerin was drawn, after separation had taken place. This method of indirect separation involved the loss of all the waste acids, and is now replaced by the following method of direct separation.

When the nitrated charge has cooled down, one of the taps at the bottom of the nitrator is connected with a lead bend, the tap opened, and the whole of the contents run off into the separating tank placed just below the level of the nitrator. The separating tank is made of stout sheet lead, and has a pyramidal bottom leading by means of a glass inspection cylinder to a branched horizontal lead pipe with earthenware stop-cocks. The top has a cover with glass windows and fitted with a fume pipe. Air pipes are led into the separator through the cover, one round the bottom of the tank, the other ending in the glass inspection cylinder. On one side of the separator is a glass inspection window, and on another side an earthenware cock situated about 4 inches below the surface of the nitroglycerin after separation has taken place. The nitroglycerin, sp.gr. 1·6, gradually separates and floats on the mixed acids, sp.gr. about 1·735. Two thermometers pass through the lid, one ending in the nitroglycerin, the other in the acids. The temperature is not allowed to rise above 17°; if it shows a tendency to rise, the air current is turned on. If the temperature cannot be reduced, and red fumes are given off, the charge

is led through a third cock at the bottom of the separator into the drowning tank. After the separation is complete, usually in about 40–45 minutes, the bulk of the nitroglycerin is run through the side tap into the 'preliminary washing tank.'

The waste acids are then run away through the bottom pipe to the 'after separating house.' When the nitroglycerin level is seen through the inspection cylinder, it is led through the second branch of the pipe into the pre-washing tank.

Any fatty acid impurities in the glycerol separate out as a vesicular scum, also containing silica, iron, and lead compounds, between the nitroglycerin and acid layers. Certain chemical and mechanical impurities also form a scum on the surface of the nitroglycerin. Any thick sludge collecting in the separator is led off through a fourth cock into the wash-water settling house.

Several suggestions have been patented to accelerate the separation. Möller, for the Dynamit Actien Gesellschaft of Hamburg (Eng. Pat. 13562, 1904), claims for the addition of a small quantity, 0·52 part per 100 glycerol, of fatty hydrocarbon or acid, or, preferably, high boiling paraffins, to the acids before nitration. Reese (Eng. Pat. 20310, 1905) attributes the slow separation to the presence of small quantities of colloidal silica and adds sodium fluoride to the nitrating acids, 0·002 part per 100 glycerol; and Haddan (Eng. Pat. 18597, 1907) claims that the nitroglycerin is rapidly separated from the nitrating acids by passing an electric current through the mixture between platinum electrodes, the gas bubbles formed during the electrolysis carrying the suspended nitroglycerin to the surface.

Nitration-separation.—In 1901 Nathan, Thomson, and Rintoul (Eng. Pat. 15983) patented an improved apparatus for the manufacture of nitroglycerin, which has been since used at the Royal Gunpowder Factory. The two operations of nitration and separation are carried out in one apparatus, and all earthenware cocks, which were a constant source of danger, are done away with, the separated nitroglycerin being displaced from the top of the apparatus by introducing waste acid below its level.

The nitrator-separator (J. Soc. Chem. Ind. 1902, 927) is a cylindrical lead vessel, with a bottom sloping in one direction, with the usual cooling coils and air pipes led in through the side just below the surface of the acid mixture. The cover, which is conical, and burnt on to the body, terminates in a small cylinder, provided with an inspection window, opening at the top into a fume pipe and also laterally into a gutter leading to the pre-wash tank. A thermometer passes through the cover. At the bottom of the tank is a pipe with three branches—one branch leads downwards to the drowning tank, another leads upwards and has two branches leading to the mixed acid and waste acid tanks respectively, the third leads to the denitrating plant.

The process is carried out as follows: After the nitrating acid is run in, and brought to the proper temperature, the glycerol injector is introduced and the nitration effected as usual. The nitric acid fumes are condensed in a Guttmann's condensing tower, about 18 lbs. of nitric acid, of sp.gr. 1·320, being recovered per ton of nitroglycerin. After the nitration is completed, the mixture is allowed to stand for a few minutes, and then waste acid is gradually run in to displace the nitroglycerin as it separates. When the separation is complete, a clear line of demarcation between the nitroglycerin and the waste acid is seen in the inspection cylinder.

The apparatus is left full until required for another nitration. In this way the life of the apparatus is largely increased, as no part of the interior is left exposed to acid fumes. Removing the nitroglycerin from contact with the acid as it separates, and the cooling during separation, increase the safety of the manufacture.

Preliminary washing.—The nitroglycerin coming from the separator is run into circular lead-lined tubs filled with water. The bottom of the tank is inclined towards a cock, and there is another cock in the side of the tank above the level of the separated nitroglycerin, for drawing off the washing waters to the 'wash-water settling house.' Compressed air is blown into the tank whilst the nitroglycerin is running in in a thin stream. A thermometer is supported in the tank and the temperature is kept below 18°. After washing for a few minutes, the nitroglycerin is allowed to separate, and the wash water is run off. More water is run in and the process repeated, any further nitroglycerin from the separator being added. The washing process is performed four times, dilute sodium carbonate solution being added in the last washing, and the temperature raised to 15°. When the preliminary washing is completed, the nitroglycerin is run down a lead-lined gutter to the 'wash house.'

The pre-wash tank now in use at Waltham Abbey has a fixed cover with a fume pipe, and has no cocks. The wash water is run off by gradually depressing a rubber funnel, connected with the outlet, into the water, and the compressed air pipe is burnt to the under side of the tank, the air holes being pierced through the bottom. This does away with any possibility of friction, and the bottom of the tank is left smooth and is readily cleaned. The washed nitroglycerin is led off through a rubber tube leading on to a gutter, which carries it to the wash house. Compressed air is blown through this rubber tube into the tank during the washing, to keep it free from unwashed nitroglycerin.

Final washing.—The final purification of the nitroglycerin to remove the last traces of acid and other impurities is effected in a lead-lined tank, over which the gutter from the pre-wash tank projects. The tank has an inclined bottom leading to the nitroglycerin draw-off cock, and is fitted with compressed air pipes for agitating the contents. The wash waters, as they separate, are run off through a pipe near the bottom, connected inside the tank by a length of indiarubber tubing with the 'skimmer,' an indiarubber-covered metal funnel that can be gradually depressed below the surface of the liquid. Cold water from the main, or warm water from an adjacent tank, can be run into the tank through indiarubber tubes. The washing tank is fixed above a large drowning tank filled with water.

The nitroglycerin is first washed with dilute

soda solution, about 2½ p.c. strength at a temperature of about 30°, hot or cold water being run in as necessary. Second, and sometimes third, washings are performed with weaker soda solution, and then lastly two washings with water only, still at the same temperature. The final washing leaves not more than 0·01 p.c. of alkali in the nitroglycerin.

The wash tank now used at Waltham Abbey is made of heavy lead without casing. The air pipe is soldered beneath the tank, there are no cocks, the skimmer is made entirely of rubber, and the nitroglycerin is run off through an indiarubber tube as from the pre-wash tank. The washing water is softened and filtered, and, like the soda solution, is stored in tanks in the charge house.

Filtration.—After the washing is complete, the nitroglycerin is usually filtered to remove moisture and suspended flocculent impurities, the operation being carried out in the washing house. The usual method is to filter through a flannel bag filled with salt, placed over a cylinder with a wire gauze bottom, into a lead-lined tank, with an inclined bottom. Sometimes two filters, one above the other, are used. The pure nitroglycerin is drawn off as required through a cock.

The present method at Waltham Abbey is to use a lead tank with a perforated false bottom, on which is placed a layer of dry sponges sewn up in flannel, and the cock is dispensed with, the rubber tube previously described being used. A sponge filter was used in the Boutmy-Faucher process.

In some factories filtering is not resorted to, but the water is removed by allowing the washed nitroglycerin to stand for some days in a warm room, when all the water rises to the surface of the nitroglycerin.

Testing.—The finished nitroglycerin is tested for moisture, alkalinity, and nitrogen content, and has to pass a specified time limit in the Abel heat test. (For a description of this test, *see* under stability tests, p. 470.)

Treating the wash waters.—All the wash waters, from washing the nitroglycerin or apparatus, which contain considerable quantities of nitroglycerin, are run down lead gutters into a large wooden tank in the wash-water settling house. The contents are kept in agitation during the day, and allowed to settle overnight. The separated nitroglycerin is run off in the morning, in the old form of tanks through a cock, in the new through an indiarubber tube, into indiarubber buckets and returned to the preliminary washing tank. The wash water is drawn off from above the level of the nitroglycerin and run into a 'labyrinth' or nitroglycerin trap, a long oblong lead tank divided into a series of compartments by partitions, with rows of holes, alternately at the top or bottom, for the water to pass through. Each partition has also one hole at the bottom, through which the deposited nitroglycerin runs and collects at the lowest point of the bottom, and is drawn off and treated like that from the wash-water settling tank. The water from the labyrinth is run into ponds, and any nitroglycerin collecting there is occasionally destroyed by detonation.

At Waltham Abbey, labyrinths are now also placed in the nitrating and wash houses, through which the wash water passes before going to the wash-water settling tank. By this means the nitroglycerin reaching the latter is materially reduced.

Secondary or *after-separation* from the waste acids. The waste acids from the separator contain a small quantity of nitroglycerin, and a further quantity is formed on standing, as already explained, from the sulphoglyceric acid. The waste acids are run into large cylindrical lead vessels, surrounded by a water jacket and fitted with cooling worms and compressed air pipes. The top of the tank is closed by a conical lid with a glass cylinder at the apex; the acids being filled in to about half-way up this tube. The cover has also a fume pipe and two thermometers, one in the nitroglycerin, the other reaching to the acid. As the nitroglycerin separates, it is removed and poured into a small lead tank containing water, which acts as a pre-wash tank.

The cooling jacket, worms, and air current are only used if the temperature rises considerably during the separation. When no more nitroglycerin separates on standing (sometimes a week is necessary), the acids are run off and treated by some denitration process, and after concentration are again used in the manufacture.

The process of separation is no longer carried out at Waltham Abbey, but the waste acids are treated by a process patented by Nathan, Thomson, and Rintoul (Eng. Pat. 3020, 1903). The patentees take advantage of the facts that the addition of a small quantity of water to the waste acids not only absorbs the suspended finely-divided nitroglycerin, but also prevents the formation of more nitroglycerin on standing. The waste acids, after standing and cooling in the nitrator-separator and removing any additional nitroglycerin that separates (this separation is much more complete than ordinarily), the quantity of acid necessary for displacing the next charge is run off into an acid elevator and forced up into the displacing tank. The remainder of the waste acids is then violently agitated, but not cooled, and 2 p.c. of water is gradually added; the acid is then run off and forced into the tank in the denitrating house.

Instead of the usual denitrating, Nobel (Fr. Pat. 351454, 1905) proposes to regenerate the waste acids by the addition of fresh acids, and claims in this way to increase the yield of nitroglycerin, and states that the process of nitration is rendered less dangerous.

Yield.—From the equation representing the formation of nitroglycerin:

$$C_3H_5(OH)_3+3HNO_3=C_3H_5(NO_3)_3+3H_2O,$$

a theoretical yield of 247 parts of nitroglycerin should be obtained per 100 parts of glycerol. Up till recently a yield of 215 p.c. was considered very good, but now yields of 229 p.c. and over are usually obtained.

A charge of 1320 lbs. of glycerol has been used at Waltham for some years. Guttmann states that it is customary in well-conducted factories to nitrate 110 kgs. of glycerol, in a mixture of 300 kgs. of nitric acid of about 93–94 p.c. monohydrate and 500 kgs. of sulphuric of 96 p.c. monohydrate. This corresponds to about 255 parts of nitric acid monohydrate, and 436·4 parts of sulphuric acid

monohydrate, or a total of 691·4 parts of acid monohydrate with 35·8 parts of water, 4·9 p.c. to each 100 parts of glycerol. He also states that the largest apparatus made in lead nitrates 680 kgs. of glycerol at one operation, whilst in America and South Africa steel apparatus with mechanical stirring gear are mostly used, some nitrating 1000 kgs. at a time. Factories using the nitrator-separator process now employ a mixture of 41 p.c. of nitric acid, 57·5 p.c. sulphuric acid, and 1·5 p.c. water, corresponding to 250 lbs. nitric acid, 350 sulphuric acid, and 9 lbs. of water for each 100 lbs. of glycerol, which gives a ratio of 6·09 of acid to 1 of glycerin.

Composition.—By sufficient dilution with copper oxide, the combustion of nitroglycerin can be carried out in the ordinary way. The nitrogen can be estimated by Dumas' method, or, better, by the nitrometer. The results of numerous analyses by different experimenters give figures very closely corresponding to the theoretical composition $C_3H_5(NO_3)_3$; and Perkin (Chem. Soc. Trans. 1889, 726) from determinations of the magnetic rotation of nitroglycerin, concludes that nitroglycerin must have its oxygen combined in the form $-O-NO_2$.

Properties.—Nitroglycerin is a heavy oily liquid; its sp.gr. at 15·6° is 1·60. When properly made from perfectly pure and colourless glycerol and acids, it is as colourless as water; but of a yellow to pale-brown colour as obtained on the commercial scale, according to the purity of the prime materials. It is neutral in reaction, and, when quite free from water, it is transparent. When pure, nitroglycerin may be kept for an indefinitely long time without decomposition. Thus Berthelot records the keeping of a specimen for 10 years, McRoberts one for 9 years, without any appearance of decomposition. But the presence of moisture, or of a trace of free acid, is able to start the decomposition of nitroglycerin; sunlight also causes it to decompose (Berthelot).

A mixture of ozone and oxygen, according to Beckerhinn, oxidises nitroglycerin at ordinary temperatures, with the formation of glyceric and nitric acids. When nitroglycerin does decompose at ordinary temperatures, the decomposition proceeds quietly, the liquid turns green, and NO_2 and CO_2 are evolved. After some time, the whole mass gelatinises, and contains much oxalic acid and ammonium salts. Nitroglycerin solidifies into long white prismatic needles, the temperature at which it solidifies varying with different samples between +8° and −11°; the frozen nitroglycerin melts again at about 11°. The time of exposure for solidifying or melting must be prolonged. Nauckhoff found that pure nitroglycerin could be cooled to as low a temperature as −40° to −50° without solidifying, though he states its true freezing-point to be 12·3°. When cooled by a mixture of solid carbon dioxide and ether, it solidifies to a glassy mass. Kast (Zeitsch. f. d. Ges. Schiess u. Sprengstoffwesen, 1906, 225) has shown that nitroglycerin exists in two allotropic forms, one solidifying at 13·2°, the other at 2·1°, the melting-points being 13·5° and 2·5° respectively. Will (Ber. 1908, 1107) gives the melting-point of the labile modification as 2·2°, and of the soluble modification as 12·2°.

Nitroglycerin is slightly volatile at ordinary temperatures, the volatility increasing with rise of temperature. According to Hess, it can be completely evaporated by continuous exposure to a temperature of 70°, and it can be distilled *in vacuó* below 100°. Will states that nitroglycerin can be completely volatilised at 160° without boiling. Champion gives the boiling-point as about 185°, but de Bryn states that this temperature is too low, and that the boiling-point is over 200°.

Although perfectly pure nitroglycerin is quite stable at ordinary temperatures, it soon begins to decompose at slightly elevated temperatures, the decomposition rapidly accelerating owing to the catalytic action of the decomposition products, so that it soon becomes dangerous. According to Guttmann, a temperature of between 45° and 50° is the critical one for nitroglycerin, the stability being practically perfect below this temperature. The decomposition is accelerated by small traces of nitrous acid; by the oxidation glyceric and oxalic acids are formed.

The velocity of decomposition of nitroglycerin, when out of contact with the products of decomposition, has been examined by Robertson (Chem. Soc. Trans. 1909, 1241). He concludes that the nitrogen is disengaged almost entirely as nitrogen peroxide, in which respect the decomposition differs from that of guncotton; that the disengagement of nitrogen peroxide proceeds in a perfectly uniform manner; that the rate of decomposition is a function of the temperature, and increases from 95° to 125°, being doubled in a rise of 5°, and that nitroglycerin has a higher rate of decomposition than guncotton under similar conditions.

Mowbray found that his nitroglycerin contracted about $\frac{1}{9}$ of its original volume on freezing.

Beckerhinn made a number of estimations of the specific gravity of Nobel's nitroglycerin, which was procured from different factories. The specific gravity of the solid nitroglycerin was taken at +10° (nearly at its melting-point); all the nitroglycerins gave very concordant values, having a specific gravity of 1·735. The specific gravity of the liquid nitroglycerin was found by numerous estimations to be 1·599; whence, in solidifying, nitroglycerin contracts about $\frac{10}{131}$ of its original volume. Consequently, Nobel's and Mowbray's nitroglycerin agree in this respect.

Beckerhinn found for the specific heat of liquid nitroglycerin (between 9·5° and 98°) the value 0·4218, and for the latent heat of fusion of solid nitroglycerin the value 33·54 heat-units.

Perkin (*l.c.*) found the magnetic rotation of nitroglycerin to be 5407.

It is inodorous, has a sweet, pungent, aromatic flavour, and even in very small quantity has toxic properties, first noticed by Sobrero. Schuchardt (Dingl. poly. J. 180, 406) tried the effect on himself of swallowing a drop of nitroglycerin. He soon experienced vertigo, headache, lassitude, and drowsiness; and an hour later, having incautiously taken more nitroglycerin, the symptoms mentioned increased in severity, and were followed by nausea and loss of consciousness. No ill effects were, however, felt next day.

The handling of nitroglycerin is followed

by similar unpleasant symptoms; but continued handling of the nitroglycerin for a day or two gives immunity from the headache. The chief symptom is usually violent headache. Fresh air, drinking black coffee, or extract of sarsaparilla, and the administration of morphine acetate, are antidotes.

Hay states that 1 gram of nitroglycerin dissolves in about 800 c.c. of water, and in 4 c.c. absolute alcohol. Will gives the solubility in water at 15° as 0·16 p.c., and the absorption of water as 0·2 p.c. It is freely soluble in methyl alcohol, ether, benzene, nitrobenzene, chloroform, acetone, glacial acetic acid, ethyl acetate, and other organic solvents.

It is practically insoluble in glycerol and in carbon disulphide. The solubility of nitroglycerin in a large number of solvents is given by Elliott, in the School of Mines Quarterly, iv. 15. Nitroglycerin is soluble in strong nitric acid, unchanged; in strong sulphuric acid it is dissolved and gradually denitrated with the formation of glyceric sulphate.

Berthelot (Sur la Force des Matières explosives d'après la Thermochimie, 1883) gives for the heat of formation of liquid nitroglycerin from liquid glycerol and nitric acid, +14·7 kgm.-degrees per molecule (227 grams) of nitroglycerin; and for the heat of formation of nitroglycerin from its elements (diamond carbon, gaseous hydrogen, nitrogen, and oxygen), +98 kgm.-degrees per 227 grams; or, +432 gram-degrees per 1 gram nitroglycerin.

Detection.—Nitroglycerin can be detected by its taste, and by absorbing a drop on bibulous paper; the drop produces a permanent greasy stain which explodes when struck by a hammer on an anvil, burns with a yellowish-green flame, with a cracking sound, or, when heated from below, explodes with a loud report. It is soluble in methyl alcohol, the solution becoming milky on the addition of water, and eventually depositing heavy oily drops. A solution of 1 vol. of aniline in 40 vols. of sulphuric acid, sp.gr. 1·84, gives a purple-red colouration with the smallest trace of nitroglycerin (Werber).

Reactions.—Of the reactions of nitroglycerin two may be mentioned. The decomposition of nitroglycerin by caustic potash was stated by Railton (Chem. Soc. Trans. 1855, 7, 222–224), to be:

$$C_3H_5(NO_3)_3+3KOH=C_3H_8O_3+3KNO_3;$$

but this was not at all justified by the results of his experiments, as only a small fraction of the nitroglycerin seems to have been decomposed, and the formation of some potassium nitrate and glycerol to have been only qualitatively determined.

Hay (*l.c.*) states that, by the action of alkalis on nitroglycerin, glycerol is not regenerated, but is oxidised at the moment of formation at the expense of the nitric acid, potassium nitrite being formed. He sums the reactions into one equation, thus:

$$C_3H_5(ONO_2)_3+5KOH=KNO_3+2KNO_2+HCO_2K+CH_3CO_2K+3H_2O$$

stating that while the oxidation products of glycerol may vary as regards their nature and proportions, the above equation expresses with approximate accuracy the course of the reaction. Berthelot (Compt. rend. 1900, 131, 519) considers that the regeneration of potassium nitrate may be taken as corresponding to that of the glycerol, and, if that is so, the production of potassium nitrite implies the simultaneous formation of a more highly oxidised product, such as glyceric aldehyde, in this way:

$$C_3H_5(NO_3)_3+3KOH=C_3H_6O_3+H_2O+2KNO_3+KNO_2.$$

Berthelot also considers that the poor stability of some samples of nitroglycerin, for which it is often difficult to account, may be attributed to the formation of glyceric aldehyde in the manufacture, produced in this way:

$$C_3H_8O_3+HNO_3=C_3H_6O_3+HNO_2+H_2O,$$

and that this nitrous acid may then form a mixed ester of the composition $C_3H_5(NO_3)_2NO_2$; both of which impurities would be difficult to detect.

In work on the hydrolysis of nitro-glycerin in alkaline solution, Silberrad and Farmer (Chem. Soc. Trans. 1906, 1759) attribute the absence of glycerol in the products to its degradation to hydroxy-acids, &c., owing to the more reactive condition of the nitric acid when first set free on hydrolysis. Nitroglycerin is acted on by potassium hydroxide in aqueous and in alcoholic solution; but, naturally, much more slowly by aqueous potash.

The reaction of nitroglycerin with alkaline sulphides, by which glycerol is formed with reduction of the NO_2 group, and not an amido derivative, is of great theoretical interest, but has not been examined quantitatively as in the case of guncotton.

Some experiments were made in 1883 by Bloxam (Chem. News, 47, 169), on the decomposition of nitroglycerin by alkaline sulphides, but more with the view of finding a safe means of disposing of nitroglycerin. He found that alcoholic solution of KHS, strong aqueous solution of K_2S, aqueous yellow ammonium sulphide, the orange-coloured solution of calcium sulphide formed by boiling flowers of sulphur and slaked lime with water, are all able (the last solution more slowly than the others) to effect the conversion of nitroglycerin into glycerol.

Combustion and detonation.—Heated rapidly to 200°, nitroglycerin inflames, and at a little higher temperature detonates with great violence (Berthelot, Sur la Force des Matières explosives).

The temperature of explosion of nitroglycerin is variously stated. Nobel states that when heated to 180°, it explodes. Hagen gives 180°–190° as the temperature of explosion of nitroglycerin; Leygue and Champion give a higher temperature. F. Hess observes that explosive substances, when slowly heated, detonate at a lower temperature than when suddenly heated. The temperature of explosion of nitroglycerin (and of explosives in general) is evidently dependent on the conditions of the experiment. McRoberts (*l.c.*) says that the explosion of nitroglycerin can be brought about by heating it to a temperature at which decomposition takes place; the decomposition itself then speedily raises the temperature to the point of explosion.

Nitroglycerin is not readily inflamed at atmospheric temperatures by contact with flame or with a red-hot body. Thus, Nobel in 1865 showed that nitroglycerin was not

inflamed when its surface was touched with a red-hot iron rod; the flame of a burning wood-shaving set on fire nitroglycerin, which burnt without explosion with a flame that went out when the source of heat was removed; and he states that burning nitroglycerin explodes only when its temperature is raised by the combustion to at least 180°.

Electric sparks will inflame nitroglycerin, but with difficulty. Abel placed two poles connected with a Ruhmkorff's coil, in some nitroglycerin and passed sparks between them; the surface of the nitroglycerin was agitated, turned black, and after half a minute the nitroglycerin exploded.

The combustion of nitroglycerin, brought about by contact with an ignited body, gives rise to nitrous vapours and a complicated reaction; it burns with a yellow flame, but without explosion properly so called, at least in the case of small quantities. But if the quantity of nitroglycerin is too large, the combustion ends in detonation. The gases produced by burning nitroglycerin (or rather, ordinary dynamite: nitroglycerin and silicious matter) have been analysed by Sarrau and Vieille. The gases were allowed to escape freely, under approximately atmospheric pressure; they had the following composition per 100 volumes of gas:—

NO	48·2	H	1·6
CO	35·9	N	1·3
CO_2	12·7	CH_4	0·3

The combustion, therefore, under these circumstances appears to be very incomplete.

In the early days of the use of nitroglycerin, Nobel effected its explosion in a borehole by means of the explosion of gunpowder (Nobel, Eng. Pat. 2359, 1863). The gunpowder was fired by a fuse, but the explosion of the nitroglycerin was uncertain and incomplete. Incomplete detonation of nitroglycerin leads to its combustion and the formation of nitric oxide and the deleterious higher oxides on coming in contact with the air. Subsequently (in 1864) Nobel exploded the nitroglycerin by means of the detonation of mercury fulminate contained in a strong copper cap, or detonator, as it is now termed, immersed in the liquid. The detonation was then complete, and the force developed much greater than when the nitroglycerin was fired by means of gunpowder.

The shock of two hard bodies capable of vibrating readily is able to cause the detonation of nitroglycerin coating the struck surfaces. Nobel noticed that a film of nitroglycerin on an anvil, struck lightly by a hammer, detonated only where struck by the hammer; but if struck heavily, the whole film of nitroglycerin detonated (McRoberts, *l.c.*). If the film be covered only with a sheet of paper, and struck, the detonation is propagated through the whole of the nitroglycerin (Désortiaux, Traité sur la Poudre, &c.). Reasoning that the blow of the hammer caused strong compression of the nitroglycerin, and raised its temperature to the exploding point, Nobel was led to try the effect of the blow caused by the detonation in the nitroglycerin of strongly confined detonating mixtures, in the hope that the blow thus given would raise the temperature of the nitroglycerin locally, as was done by the blow of the hammer, and would thereby cause its explosion. He eventually (in 1864) found that the detonation of nitroglycerin could be rendered certain by the use of mercury fulminate contained in a strong copper cap (McRoberts, *l.c.*). This idea of firing an explosive by initial detonation was one of the greatest improvements ever made in the use of explosives. It made the use of nitroglycerin as a blasting agent practicable, was subsequently applied by Abel and Brown to guncotton, and is now used for firing all high explosives.

It has been mentioned that the detonation of nitroglycerin is readily caused when it is subjected to the shock of two hard sonorous bodies, as that of iron on iron. The shock of copper on copper is believed to be less dangerous, and that of wood on wood still less so; but explosions of nitroglycerin have been caused by such shocks (Berthelot, Sur la Force des Matières explosives, &c.). The sensitiveness of nitroglycerin to friction and percussion increases with the temperature.

Frozen nitroglycerin is less readily detonated by a blow, or by the detonation of mercury fulminate, than when in the liquid state. This was to be expected, as detonation results in both cases from the transformation into heat of the kinetic energy imparted to the particles of nitroglycerin—heat sufficient at the part struck to raise the temperature of the nitroglycerin to the temperature of explosion; and to raise frozen nitroglycerin to that temperature, more heat would be required than in the case of the liquid, on account of the heat absorbed in melting the solid nitroglycerin. Thus, Beckerhinn states (Sitz. W. 72 and 73, in abstract in the Jahresbericht der chemischen Technologie, 1876, 22, 481–487) that quantities of mercury fulminate which would have detonated liquid nitroglycerin with certainty, did not detonate crystallised nitroglycerin; also, that when a flat anvil of Bessemer steel was thinly coated with liquid and with solid nitroglycerin, and a wrought-iron weight allowed to fall on it, the mean height of fall required to effect detonation was for liquid nitroglycerin 0·78 metre (2·6 feet), for frozen nitroglycerin 2·13 metres (7 feet). McRoberts (*l.c.*) states that a detonator containing even so much as 1 gram of mercury fulminate does not effect the detonation of thoroughly frozen nitroglycerin, while 0·1 gram of fulminate will detonate liquid nitroglycerin.

The products of the detonation of nitroglycerin are stated to be those of complete combustion, and the equation representing the change is given as:

$$2C_3H_5(NO_3)_3 = 6CO_2 + 5H_2O + 6N + O.$$

Sarrau and Vieille (Compt. rend. 90, 1060) state that experiment shows that the decomposition of nitroglycerin in a closed vessel is represented by the above equation; but no analysis of the gases is given.

Calculated from the above equation, nitroglycerin contains an excess of 3·52 p.c. oxygen (per 100 nitroglycerin) above that required for complete combustion, and 100 grams of nitroglycerin would be converted into 58·15 grams CO_2, 19·83 grams H_2O, 3·52 grams O, and 18·50 grams N.

Nobel has calculated that 1 vol. of nitroglycerin on explosion generates about 1200 vols. of gases, calculated to normal temperature and pressure, and that the heat generated expands the gases to nearly eight times this volume, and concludes that the explosive force of nitroglycerin is 13 times as great as that of an equal volume of gunpowder.

The quantity of heat evolved by the total combustion of nitroglycerin, as represented in the above equation, is given by Berthelot (Sur la Force des Matières explosives, &c.), for 227 grams nitroglycerin and in Calories (kgm.-degree units), as follows :—

The water liquid, constant pressure, +356·5 Calories ; constant volume, +358·5 Calories.

The water gaseous, constant pressure, +331·1 Calories ; constant volume, +335·6 Calories.

Or, per 1 kilogram of nitroglycerin :

The water liquid, constant pressure, +1570 Calories ; constant volume, +1579 Calories.

Sarrau and Vieille obtained, by experiment, +1600 Calories.

The volume (at 0° and 0·76 metre pressure) of the gases produced by the detonation of nitroglycerin, calculated from the equation given above, is 714 *litres* per 1 kilogram nitroglycerin, the water taken as gaseous ; or 1142 litres gas (under the given conditions) per 1 litre nitroglycerin. The calculated volume of the permanent gases (*i.e.* the water taken as liquid, tension of aqueous vapour at 0° disregarded) at 0° and 0·76 metre is 467·5 litres per 1 kilogram of nitroglycerin, or 748 *litres* per 1 litre of nitroglycerin. Berthelot mentions that Sarrau and Vieille found experimentally the volume of permanent gases to be 465 litres at 0° per 1 kilogram nitroglycerin. The gases at the moment of detonation are greatly expanded by the heat of the combustion ; according to an early statement of Berthelot (in 1871), the gases are expanded to eight times their volume at 0°.

It will be convenient to requote the numbers obtained by Noble and Abel (Fired Gunpowder, No. 2, Trans. Roy. Soc. 1880) with Waltham Abbey fine-grain gunpowder and ordinary English mining powder.

One kilogram perfectly dry powder gave on explosion :

	W. A. fine-grain	Mining powder
Quantity of heat in Calories (kgm.-degrees) . .	738·3	516·8
Permanent gases in litres at 0° and 0·76 metre . .	263·1	360·3

The statements as to the relative power of nitroglycerin and ordinary blasting powder as blasting agents vary ; partly, no doubt, on account of differences in the rocks blasted, as nitroglycerin is most effective in a compact rock, offering equal resistance in all directions to the gases produced by the explosion. Thus, Trauzl (quoted by Berthelot) stated in 1870 that nitroglycerin used for blasting in quarries produced five to six times the effect of an equal weight of blasting powder ; and for equal volumes the difference would be much greater. The effects produced are those of dislocation, specially dependent on the initial pressures. Schwanert (quoted by Böckmann) states that the mean blasting power of nitroglycerin may be taken as being 3·5 to 4 times greater than that of ordinary blasting powder ; equal weights being in all probability intended.

The velocity of the propagation of detonation in liquid nitroglycerin has been determined by Abel (Trans. Roy. Soc. 1874, 385, 386). The length of nitroglycerin used was 14 feet, the weight 3 ozs. per foot of the train. The liquid was contained in a V-shaped trough of thin sheet metal ; at intervals of 2 feet, fine insulated copper wires crossed the trough (having been passed through, and cemented into, small holes in the sides of the trough) sufficiently near the bottom to be covered by the nitroglycerin. The velocities were measured by Noble's chronoscope ; the mean rate of detonation was found to be 5305 feet (1612 metres) per second, or little more than one-fourth the rate of detonation of cylinders of compressed guncotton in a continuous row.

Use.—Nitroglycerin, as such, is no longer used as an explosive. It was at one time used to a large extent, especially in America ; for instance, about 70 tons of Mowbray's nitroglycerin, transported in the frozen state, was used in the construction of the Hoosac Tunnel in Massachusetts in 1874. Its use was prohibited in England in 1874, and then died out in Europe, but it was employed in America for some years afterwards. Since the invention of nitrogelatin, there is no incentive to use raw nitroglycerin, as the former is as powerful an explosive as the latter.

Dynamites.

It has been already mentioned that the serious accidents which, in 1864–66, attended the transport or manufacture of nitroglycerin were followed by a reaction against its use, and in this country by a prohibitive Act in 1869. To render its transport safe, Nobel introduced the use of a solution of nitroglycerin in wood-spirit (methyl alcohol) ; a solution which is not explosive, and from which the nitroglycerin was to be separated by precipitation by water at the place where it was to be used. This method of protection was soon abandoned, as the separation of the nitroglycerin was troublesome, and at low temperatures it crystallised out from the solution. A further disadvantage in the use of nitroglycerin is that it may run from the borehole into fissures in the rock, escape detonation, and either burn and give off deleterious oxides of nitrogen, or, if unburned, be a grave source of danger on removing the rock. Attempts were made to overcome this difficulty by lining the borehole with clay. Subsequently Nobel succeeded in making the use of nitroglycerin comparatively safe by employing porous substances to absorb the liquid ; to these preparations he gave the name Dynamite.

As he had been experimenting with a mixture of nitroglycerin and gunpowder, Nobel at first used charcoal as an absorbent, and various other substances were subsequently tried, but he found 'kieselguhr,' or so-called infusorial earth, to be the best absorbent of nitroglycerin (Eng. Pat. 1345, 1867). Nobel originally intended that the nitroglycerin should be separated out again for use, but he subsequently found that the dynamite itself could be more readily detonated than the liquid nitroglycerin.

The term 'dynamite' has now a more

general significance. It is applied to all mixtures of nitroglycerin with solid substances, which absorb and retain it under ordinary conditions of storage, whatever the nature of the latter; but when used specifically, 'Kieselguhr Dynamite No. 1' is meant.

The absorbent material is known as the 'base' or 'dope,' and dynamites may be classified according to the nature of the base into: (1) those with an inert base; (2) those with a combustible base; and (3) those with an explosive base. The last class includes those with bases which are explosive mixtures (nitrate, chlorate, perchlorate, &c.), and those which are explosive compounds, either of the 'nitro-' or 'nitrate' class. In the last class it will be convenient to include blasting gelatin and gelatin-dynamite, although the nitrocelluloses have not yet been considered.

1. *Dynamites with an inert base.*

Dynamite No. 1 or Kieselguhr dynamite. Kieselguhr dynamite contains from 70 to 80 p.c., usually 75 p.c., of nitroglycerin. (Dynamites with less than 30 p.c. of nitroglycerin will not explode.) A small quantity of alkali, formerly 1·5 p.c. ammonium carbonate, now 0·5–1 p.c. anhydrous sodium carbonate, is usually added to neutralise any free acid that may develop on storage; but alkali is not always added.

Kieselguhr. The earth is found in several places; that first used was obtained from Oberlohe in Hanover, where there is an extensive bed of it. It consists of the frustules of diatoms, and is mainly silica; Beckerhinn examined some kieselguhr, and found it to contain 95 p.c. SiO_2, and its specific heat to be 0·2089. The kieselguhr is moderately calcined to remove water and organic matter, then ground and sifted. The dried kieselguhr is packed in canvas bags and stored in a dry atmosphere. Dynamite made with a guhr containing more than about 0·5 p.c. of water will exude nitroglycerin on storage.

The kieselguhr used at Ardeer is obtained from Aberdeenshire; it absorbs three or four times its weight of nitroglycerin, retaining it under considerable pressure. The calcined material contains about 98 p.c. SiO_2 (McRoberts, *l.c.*).

Manufacture.—The nitroglycerin and kieselguhr are mixed by hand in shallow lead tanks. The guhr is weighed out into the tank, the weighed charge of nitroglycerin poured over it from a bucket of indiarubber, guttapercha, or similar material, the ingredients kneaded, and then rubbed through the meshes of a coarse wire sieve, to complete the admixture. Sometimes two sieves are used, a coarse one with about 3 meshes to the inch, and a finer one with 7 meshes to the inch. The dynamite is then in the form of plastic grains. These must neither be dry enough to crumble nor decidedly greasy, or the cartridges will not be satisfactory. If the guhr be too absorbent, the mixture will be too dry for pressing, and in this case a small quantity of barium sulphate is usually added, or, sometimes, mica, talc, or ochre up to 8 p.c. replacing an equal weight of kieselguhr.

The dynamite cartridges are small cylinders, in which form they are squeezed out from the cartridge machine; the latter is a cylindrical metal tube, in which a wooden piston works, pressure being applied to the piston by means of a lever. One end of the tube is terminated by a funnel-shaped piece with orifice of the same diameter as that of the cartridges. The cartridges, usually either $\frac{3}{4}$ or $\frac{7}{8}$ of an inch in diameter, but sometimes 1· inch, are sent out wrapped in parchment- or paraffined paper.

Properties.—Kieselguhr dynamite is a plastic, pasty substance, the colour of which varies from pink or grey to a dark-brown, according to the colour of the base, and whether ochre has been added or not.

Water separates the nitroglycerin from ordinary kieselguhr dynamite. The specific gravity of dynamite is about 1·6. When unfrozen dynamite is set fire to by application of flame, the nitroglycerin burns quickly with yellowish flame, giving off nitrous fumes. Large quantities can thus be burnt without explosion; but eventually the unburnt portion becomes heated to the temperature of explosion, and explodes. When exposed to a slowly rising temperature, dynamite fires at about 180°. It can be safely destroyed by laying it in a long thin train, pouring any waste oil over the train, and firing it. Dynamite usually freezes at about 4°. Frozen dynamite burns very slowly, thawing preceding combustion. When a comparatively small heap of frozen dynamite cartridges is set fire to, an explosion often ensues. Like nitroglycerin, frozen dynamite is less sensitive to shock than unfrozen, and the ordinary detonator does not explode thoroughly frozen dynamite, although one-tenth part of the detonator charge is sufficient to cause the detonation of unfrozen dynamite (McRoberts, *l.c.*). Since frozen dynamite is comparatively useless as an explosive, it must be thawed or 'tempered' before being used, and this only takes place at temperatures considerably above the freezing-point. Thawing is done in special warming pans, in which the vessel containing the dynamite is surrounded by a jacket containing warm water (at a temperature not above 70°) and this in turn by a layer of felt or other non-conducting material. Dynamite is less sensitive to shock than nitroglycerin; the sensitiveness increases with the percentage of nitroglycerin in the dynamite, and (like explosives in general) with increase of temperature. It is detonated by the shock of iron on iron, or of iron on stone, but not by that of wood on wood. Dynamite between steel and steel, according to Hess, requires a blow of 0·75 kgm.-metre for detonation; when frozen it requires 1 kgm.-metre. In the unfrozen state it is readily detonated by the shock of a rifle-bullet; Berthelot states that it detonates under the direct blow of the bullet when fired at 50 metres' (164 feet) distance, and even more. Placed on an anvil and struck, it requires a smart blow of the hammer to cause an explosion, and then only the portions directly struck detonate, the rest being scattered without exploding. The silicious skeletons of the frustules of diatoms composing the kieselguhr form separate receptacles for the nitroglycerin, and have a cushioning effect towards a mechanical blow, the energy thereby imparted being divided between the absorbent and the nitroglycerin. Berthelot (Sur la Force

des Matières explosives, &c.) remarks that dynamite is less crushing in its action than nitroglycerin, because the heat evolved on its detonation is shared between the products of the explosion and the inert substance, the latter by its presence lowering the temperature. Thus, the specific heat of kieselguhr (0·2) is almost the same as the mean specific heat of the gaseous products of explosion of nitroglycerin at constant volume; in the case of No. 1 dynamite with 25 p.c. kieselguhr, in a vessel completely filled by it, and too strong to be burst by its detonation, the kieselguhr would lower the temperature of the gases by one-fourth, and consequently diminish the initial pressure. In blasting, the condition of the gases of explosion would be intermediate between constant volume and constant pressure. In using dynamite, its detonation is effected by means of the explosion of a mercury fulminate detonator and fired by an electric current or by means of Bickford fuse, the cap being embedded in the dynamite. The detonator must be sufficiently powerful to ensure complete detonation of the nitroglycerin, or nitrous fumes will be generated in the mine workings. The detonator supplied for the purpose by Nobel's Explosive Company contains about 0·5 gram of a mixture of 70 p.c. mercury fulminate and 30 p.c. potassium chlorate.

The velocity of propagation of the detonation of this dynamite was found by Abel (Trans. Roy. Soc. 1874, 384, 385) to be 20,000 feet per second. The experiment was made with half-inch cartridges of dynamite in a continuous train of 42 feet, the rate being measured at intervals of 6 feet by means of Noble's chronoscope.

Abbot (U.S. Engineers) obtained from his experiments (Report upon a System of Submarine Mines, &c., 1881, 111) the remarkable result that the intensity of action of ordinary kieselguhr dynamite containing 75 p.c. nitroglycerin, fired under water, is greater than that of nitroglycerin. Thus, in a series of experiments he found the intensity of action of nitroglycerin detonated under water to be 81, that of an equal weight of dynamite being 100. To confirm the results, nitroglycerin was mixed, under Abbot's supervision, with prepared kieselguhr into dynamite of 75 p.c., and shots were immediately fired under water with this dynamite, and with the nitroglycerin from which it had been made. The mean of five shots gave the intensity of the liquid nitroglycerin as 85, that of the dynamite being 100 (equal weights compared). Abbot remarks that in blasting hard rock, nitroglycerin is admitted to be by far stronger than dynamite; in explanation he supposes that in dynamite the particles of kieselguhr slightly retard chemical action, and that the resistance opposed by water being of a slightly yielding character, may exact more time than is required by pure nitroglycerin. According to Abel's experiments, however, the rate of detonation of dynamite is very much quicker than that of liquid nitroglycerin,—a result agreeing with those of Abbot's experiments, but not with his explanation of them. It is true, as Abel points out, that the determination of the rate of detonation of liquid nitroglycerin (which was contained in an open trough) was likely to be given too low, owing to the tendency of the liquid particles to escape from the blow of the detonation, and that experiments with *confined* nitroglycerin would be desirable.

Tested by the lead cylinder method, the intensity of action of nitroglycerin is 1·4 when that of No. 1 dynamite is unity. Von Pischoff, in Austria in 1869, comparing the relative values of dynamite and gunpowder, found that the former was roughly three times as strong as gunpowder, variations from 2·4 to 3·3 being obtained according to the nature of the rock. The nature of the kieselguhr has some influence on the explosive power of the dynamite; the guhrs containing most tubular structures not only absorb better, but each of these tubes offers resistance on detonation, and confers greater intensity of action by its tamping effect.

Dynamite of Vonges. Instead of kieselguhr, in France a similar silicious earth called *Randanite* (from Randan in the Puy-de-Dôme) is used as the absorbent in the Vonges make of dynamite. Tripoli and the ashes of Boghead coal have also there been employed as substitutes for kieselguhr. Analysis of a modern sample gave 75 p.c. nitroglycerin, 20·8 p.c. randanite, 3·8 p.c. quartz, and 0·4 p.c. magnesium carbonate. The American *Giant powder No. 1* is dynamite No. 1 containing 0·5 p.c. sodium carbonate.

Magnesia alba has also been used as the absorbent of nitroglycerin, its absorptive power being said to exceed that of kieselguhr, and it is also said to increase the intensity of action of the dynamite by the expulsion of its carbon dioxide. The combination was proposed in 1879, by Jones of Caerphilly, and named *Nitromagnite* or *Dynamagnite*. Its manufacture was abandoned, as it was decided that it conflicted with the existing patents of Nobel.

Modifications of kieselguhr dynamite have been proposed, more especially on the Continent, with a view of rendering it safe to use in fiery mines: various additions, such as salts containing much water of crystallisation, being made to reduce the temperature of the flame. Such explosives are naturally less powerful than ordinary dynamite.

In *Wetter dynamite*, proposed by Müller of the Cologne dynamite factory (Eng. Pat. 12424, 1887), crystallised sodium carbonate is used. Composition 52 p.c. nitroglycerin, 14 p.c. kieselguhr, and 34 p.c. soda crystals.

Grisoutite contains magnesium sulphate. It is composed of 53 p.c. nitroglycerin, 14·5 p.c. kieselguhr, and 32·5 p.c. magnesium sulphate.

Nobel Ardeer powder is a dynamite of this class, for although it contains nitre, it has no added combustible. Composition: 33 p.c. nitroglycerin, 49 p.c. magnesium sulphate, 13 p.c. kieselguhr, and 5 p.c. nitre.

Mica powder (Abbot, Report upon a System of Submarine Mines, &c., 93, 110) consists of finely divided mica scales and nitroglycerin. It was made in the United States by Mowbray, and was largely used, with good results, in completing the Hoosac Tunnel. The nitroglycerin adheres to the scales, but is not absorbed by them. Mowbray claimed that, owing to the very large surface exposed, a more instantaneous reaction is secured than with liquid nitroglycerin. He estimates the interstitial spaces at one-fourth the volume of the powder when tolerably well rammed.

Abbot experimented with a No. 1 mica powder containing 52 p.c. nitroglycerin, and with a No. 2 containing 40 p.c.; the charges being detonated under water. He found the intensity of action of No. 1 to be 83, of No. 2 to be 62; that of liquid nitroglycerin, in the same circumstances, being 81, and that of kieselguhr dynamite No. 1, containing 75 p.c. nitroglycerin, being 100 (equal weights compared). The result is remarkable, as it gives the intensity of action of the nitroglycerin in mica powder as double that of an equal weight of liquid nitroglycerin.

2. *Dynamites with a Combustible Base.*

Carbodynamite is a preparation introduced by Messrs. W. D. Borland and W. F. Reid (Eng. Pat. 758, 1886). It consists of 10 p.c. cork charcoal, which has absorbed 90 p.c. nitroglycerin. Sodium or ammonium carbonates and water may or may not be present.

It is claimed for carbodynamite that it can be kept under water for weeks without losing its nitroglycerin, which would be a great advantage over kieselguhr dynamite.

As was to be expected from the high percentage of nitroglycerin, the intensity of action of carbodynamite is very high—much higher than that of kieselguhr dynamite. In one variety of carbodynamite, water was added to render the explosive safe enough to use in fiery mines. Another variety, No. 2, belongs to the third class of dynamites, as it contains 80 p.c. nitroglycerin, 14 p.c. nitre, and 6 p.c. cork charcoal.

Grisoutite. Another form of this safety explosive contains wood meal as the absorbent, instead of kieselguhr. Composition: 44 p.c. nitroglycerin, 12 p.c. wood meal, 44 p.c. magnesium sulphate.

Forcite is the name given to explosives manufactured in various grades by the American Forcite Company, New Jersey. The original patent (of 1881) describes forcite as consisting of nitroglycerin incorporated with unnitrated gelatinised cellulose and with nitre. Cotton or other form of cellulose was to be purified chemically as in paper making, to be reduced to powder and to be subjected to the action of high-pressure steam, by which it was converted into a gelatinous mass. It was then allowed to cool, and was to be incorporated at 40° with nitroglycerin and with nitre. One of the best compositions was stated to be: nitroglycerin, 75 p.c.; gelatinised cotton, 7 p.c.; nitre, 18 p.c. Dextrin and ordinary cellulose in powder might partly replace the gelatinised cotton.

Forcite is described as a hard plastic substance, having very much the appearance and toughness of indiarubber. Economy, non-exudation of nitroglycerin, and imperviousness to water, were claimed for it. There is considerable variation in the statements as to the composition of forcite; thus, in one kind the gelatinised nitroglycerin is said to be incorporated with a mixture composed of sodium nitrate, wood tar, a little sulphur and wood pulp. It is made in various grades containing different amounts of nitroglycerin. Eissler states that the type mostly in use (in the United States, and in 1886), and which possesses the best qualities, is the No. 1, containing from 65 to 85 p.c. nitroglycerin; also that the quantity of nitroglycerin in different grades varies from the large amount mentioned to only 20–25 p.c. He states that quadruple-force caps are employed to explode forcite.

Abbot (U.S. Engineers) made estimations of the intensity of forcite exploded under water; the intensity varied with the grade, between 88 and 133, ordinary kieselguhr dynamite No. 1 being 100 (Addendum II. to Report on Submarine Mines). Belgian and other continental makes of forcite contain nitrocellulose, and come in class 3 of dynamites.

Forcite antigrisouteuse No. 2 has a similar composition to 'grisoutite.'

Rhenish dynamite consists of 75 p.c. of a solution of naphthalene in nitroglycerin, 25 p.c. of kieselguhr, and a little chalk or barium sulphate.

3. *Dynamites with an Explosive Base.*

Kieselguhr dynamite is much too violent and local in its effects to be used in most mining operations, such as in coal-mines or slate and granite quarries, where great power and shattering effects are undesirable. As the force cannot be moderated by reducing the proportion of nitroglycerin without increasing the difficulty of detonation, the dynamites with an explosive base have gradually superseded it for mining purposes.

i. *Dynamites with a Potassium Nitrate Mixture Base.*

Dynamite No. 2 is black in colour, and is milder and slower in its action than No. 1. It was introduced to imitate the explosive characteristics of gunpowder. It consists of (not more than) 18 p.c. of nitroglycerin, uniformly mixed with 82 p.c. of a pulverised preparation, composed of 71 p.c. potassium nitrate, 10 p.c. charcoal, 1 p.c. paraffin. Scarcely used at all in this country.

Rend rock is a modern modification of 'Lithofracteur,' having the composition 40 p.c. nitroglycerin, 40 p.c. nitre, 13 p.c. wood pulp, and 7 p.c. pitch.

Atlas powders B+ and C+, as used in the construction of the Panama Canal, contained *B+*, 60 p.c. nitroglycerin, with wood pulp and nitre, and 3 p.c. of magnesia; *C+*, 45 p.c. nitroglycerin, with wood pulp and nitre and 2 p.c. of chalk.

Some forms of *Wetter dynamite* contain a similar mixture. A sample from Wittenberg contained 25 p.c. nitroglycerin, 35 p.c. mixed nitrates of potassium and barium, and 40 p.c. wood meal.

Carbite, a French dynamite of this class, contains 25 p.c. nitroglycerin, 34 p.c. potassium nitrate, 1 p.c. barium nitrate, 38·5 p.c. flour, 1 p.c. powdered bark, and 0·5 p.c. sodium carbonate.

Carbonite, made by Bichel and Schmidt of Schlebusch, is claimed to be a safe explosive for use in fiery mines. It contains 25–27 p.c. nitroglycerin, 30–36 p.c. of a mixture of potassium and barium nitrates, and 40–43 p.c. starch and wood meal, with 0·5 p.c. sodium carbonate, and 0·5 p.c. of sulphuretted benzene. An actual sample contained 25 p.c. nitroglycerin, 34 p.c. potassium nitrate, 1 p.c. barium nitrate, 10 p.c.

wood meal, 29·5 p.c. rye flour, and 0·5 p.c. sodium carbonate.

Stonite, also made by Bichel and Schmidt, consists of 68 p.c. nitroglycerin, 20 p.c. kieselguhr, 8 p.c. potassium nitrate, and 4 p.c. wood-meal.

Kynite is a safety explosive of similar composition to carbonite. One analysed sample contained 25 p.c. nitroglycerin, 35 p.c. barium and potassium nitrates, and 40 p.c. starch and wood meal. As licensed, *Kynite condensed* contains 24–26 p.c. nitroglycerin, 32·5–35 p.c. starch, 2·5–3·5 p.c. wood meal, 31·5–34·5 p.c. barium nitrate, and 0–0·5 p.c. calcium carbonate; the explosive to be used only in a non-waterproofed parchment-paper wrapper.

Dualine contains 50 p.c. nitroglycerin, 20 p.c. potassium nitrate, and 30 p.c. sawdust.

ii. *Dynamites with a Sodium Nitrate Mixture Base.*

Judson powder is an explosive which has been largely used in the United States in quarrying and railway work; it is a roughly made sodium nitrate blasting powder, the grains of which are coated with nitroglycerin. The grade R.R.P. is the one most commonly used, and is sold at the price of common saltpetre blasting powder; it is composed of sodium nitrate 64 p.c., sulphur 16 p.c., cannel coal 15 p.c., nitroglycerin 5 p.c. The nitrate, sulphur, and coal are thoroughly mixed in fine powder, and the mixture heated on a pan by steam under pressure, and constantly stirred until the sulphur melts. The mass is then allowed to cool, when it is found agglomerated in grains, which are sorted by sieves and coated with nitroglycerin by stirring. The object of coating the powder grains with the nitroglycerin was to promote the quickness of explosion. It is exploded by the detonation of a primer of Giant or Atlas powder. Abbot (*v. supra*) found the intensity of action of the R.R.P. grade, exploded under water, to be 38–39, kieselguhr dynamite No. 1 being 100. Other brands now in use with their percentages of nitroglycerin are: F. 10 p.c., F.F. 15 p.c., F.F.F. 20 p.c., Dbl. Ex. 27 p.c., and Tpl. Ex. 33 p.c.

Giant powder No. 2, supplied by the Atlantic Giant Powder Company, and composed of nitroglycerin 36 p.c., potassium or sodium nitrate 48 p.c., sulphur 8 p.c., resin, powdered coal or charcoal 8 p.c. Exploded under water, its intensity of action was 83 p.c. of that of dynamite No. 1. A more modern composition is 40 p.c. nitroglycerin, 40 p.c. sodium nitrate, 8 p.c. kieselguhr, and 6 p.c. sulphur. There are six or more other brands with percentages of nitroglycerin varying from 20 to 50.

Vigorite contains 30 p.c. nitroglycerin, 60 p.c. sodium nitrate, 5 p.c. charcoal, and 5 p.c. sawdust.

Vulcan powder was used in some of the earlier blasting work at Hellgate, New York Harbour. The usual trade explosive, of the composition nitroglycerin 30 p.c., sodium nitrate 52·5 p.c., charcoal 10·5 p.c., sulphur 7 p.c., fired under water gave intensity = 78 p.c.; and a No. 2 sample containing 35 p.c. nitroglycerin, gave intensity = 82 p.c. compared with the usual standard (Abbot).

Lithofracteur, invented by Engels, and made by Kiebs & Co., of Cologne, is said to consist of 55 p.c. nitroglycerin, 21 p.c. kieselguhr, and 24 p.c. of charcoal (bran or sawdust), barium nitrate, bicarbonate of soda, peroxide of manganese, and sulphur; the latter ingredients in such proportion as to give the highest temperature and greatest quantity of gas. Stated to be nearly equal in intensity to kieselguhr dynamite No. 1 (Böckmann, Die explosiven Stoffe). One sample gave on analysis 52 p.c. nitroglycerin, 30 p.c. kieselguhr, 12 p.c. powdered coal, 4 p.c. sodium nitrate, and 2 p.c. sulphur; another sample contained 70 p.c. nitroglycerin, 23 p.c. kieselguhr, 2 p.c. powdered coal, and 5 p.c. barium nitrate. This explosive was formerly on the list of 'authorised' explosives, but is not now used in this country.

Lignin dynamites. In the United States, large quantities of nitroglycerin preparations are used in rock-blasting, consisting of nitroglycerin absorbed by a mixture of wood pulp (or of sawdust in some of the lower grades) and a nitrate, usually sodium nitrate. For the complete combustion of wood with formation of sodium carbonate, about 2·5 parts by weight of sodium nitrate are required to 1 of wood. General Abbot, in 1885, says, 'Development in the United States is at present most actively directed to the dynamites with explosive bases, economy being sought in making use of the least possible percentage of nitroglycerin.'

Atlas powder may be taken as a type of several American preparations. It consists essentially of sodium nitrate, wood pulp (or sometimes of sawdust), magnesium carbonate, and nitroglycerin. A series of grades is made, containing 75 p.c. to 20 p.c. nitroglycerin.

Abbot experimented with two grades, A and B, of Atlas powder; they were composed of:

	Grade A	Grade B
Sodium nitrate	2	34
Wood fibre	21	14
Magnesium carbonate	2	2
Nitroglycerin	75	50

Fired under water, the intensity of grade A was just that of an equal weight of kieselguhr dynamite No. 1 (75 p.c. nitroglycerin); whilst the intensity of Atlas B was = 99 p.c. of the same standard (Abbot, Addendum II. to Report on Submarine Mines). Grade A shows no economy in nitroglycerin over kieselguhr dynamite of the same percentage, probably owing to the too low ratio of sodium nitrate to wood fibre. Grade B, in which the ratio of nitrate to wood is that of complete combustion, shows a great economy in nitroglycerin.

Abel found (by the lead cylinder method) the intensity of an Atlas powder of American make to be 106, kieselguhr dynamite No. 1 being = 100.

Hercules powder has essentially the same composition as Atlas powder. Several grades of it are made in the United States, containing from 75 p.c. to 20 p.c. nitroglycerin. Some years since, two grades were tried by Abbot, and fired under water; their composition and intensity of action were:

	No. 1	No. 2
Nitroglycerin	77 p.c.	42·0 p.c.
Sodium nitrate	1 „	43·5 „
Wood pulp	2 „	11·0 „
Magnesium carbonate	20 „	3·5 „
Intensity	106 „	83·0 „

(Kieselguhr dynamite No. 1 being = 100).

Similar American lignin dynamites of this class are the various *Giant powders*, with quantities of nitroglycerin, varying from 20–50 p.c. (exclusive of the giant powders 1 and 2 already mentioned); *Safety nitro powder*, containing 69 p.c. nitroglycerin, 18 p.c. sodium nitrate, and 13 p.c. wood pulp; *Hecla powder*, made in seven grades, containing 75–20 p.c. nitroglycerin; *Miner's friend*, and others.

Rhexite is manufactured by the Borkenstein Co. in Styria. One sample contained 64 p.c. nitroglycerin, 18 p.c. sodium nitrate, 11 p.c. decayed wood, and 7 p.c. wood meal.

Rexite as licensed by the Home Office, the explosive contains 64–68 p.c. ammonium nitrate, 13–16 p.c. sodium nitrate, 6·5–8·5 nitroglycerin, 6·5–8·5 trinitrotoluene, 3–5 p.c. wood meal, and 0·5–1·5 p.c. moisture, used in a stout paper case waterproofed with ceresin and wax.

Some forms of *Carbonite* contain sodium nitrate instead of nitre. *Coal carbonites I. and II.* contain respectively 25 and 30 p.c. nitroglycerin, 30·5 and 24·5 p.c. sodium nitrate, 39·5 and 40·5 p.c. rye flour (containing about 2·5 p.c. water), and 5 and 5 p.c. potassium dichromate. *Carbonite I.A* contains sodium chloride instead of potassium dichromate.

Phœnix powders resemble the above forms of carbonite. They are manufactured in various brands:

	I.	II.	III.
Nitroglycerin	30	25	25
Sodium nitrate	30	1	35
Barium and potassium nitrates	—	34	—
Rye flour	40	—	40
Wood meal	—	40	—
	100	100	100

Sometimes a little nitrocotton is added to gelatinise the nitroglycerin.

iii. *Dynamites with an Ammonium Nitrate Mixture Base.*

Ammonia dynamite was a nitroglycerin preparation proposed and patented in 1872 by Ohlson and Norrbin, which consisted of nitroglycerin 10 p.c. to 20 p.c., ammonium nitrate 80 p.c., charcoal 6 p.c. The material is deliquescent, and paraffin was added to the mixture to waterproof it. Berthelot states that practical tests have shown ordinary dynamite of 60 p.c. nitroglycerin, and the preparation consisting of 75 p.c. ammonium nitrate, 3 p.c. charcoal, 4 p.c. paraffin, and 18 p.c. nitroglycerin, to be approximately equal in intensity of action.

In 1873 the British Dynamite Co. (now Nobel's Explosive Co.) submitted two samples of ammonia dynamite to the special War Office Committee on Guncotton, &c., containing respectively 18 and 13 p.c. nitroglycerin, 75 and 70 p.c. ammonium nitrate, 4 and 7 p.c. paraffin, and 3 and 10 p.c. charcoal dust. They were unfavourably reported on, on account of the possibility of exudation of nitroglycerin on storage, due to the deliquescent nature of the ammonium nitrate. As permitted for manufacture in this country, Nobel's ammonia powder had the composition:

	No. 1	No. 2
Ammonium nitrate	82–86 p.c.	78–82 p.c.
Nitroglycerin	7–9 „	9–11 „
Wood meal	6–8 „	8–10 „
Moisture	0·5–2 „	0·5–2·5 „

A recent sample of *Pulverulent ammonium dynamite* contained 20 p.c. nitroglycerin, 25 p.c. ammonium nitrate, 36 p.c. sodium nitrate, and 19 p.c. dry rye flour.

Most modern dynamites containing ammonium nitrate also contain nitrocotton, which serves to protect them from the action of moisture.

iv. *Dynamite with a Chlorate Mixture Base.*

Although the substitution of a chlorate for a nitrate mixture, as an absorbent for nitroglycerin, increases the power of the resultant explosive, it adds to the cost, and the explosives possess the dangerous properties inherent in chlorate mixtures. They are not used in this country.

An early example of this class of dynamite was proposed by Horsley, in 1872, in which a mixture of finely ground gall nuts and potassium chlorate, in the proportion of 1 to 3, was impregnated with 20 p.c. nitroglycerin.

Some modern grades of the American *Hercules powders* contain potassium chlorate and sugar instead of the older wood pulp, their composition being: 40–75 p.c. nitroglycerin, 1–16 p.c. sugar, 1–3·5 p.c. potassium chlorate, 2–30 p.c. potassium nitrate, and 10–20 p.c. magnesium carbonate.

v. *Dynamites containing a Nitro Derivative.*

Castellanos powder was an early dynamite of this class which contained nitroglycerin, nitrobenzene, fibrous material, and kieselguhr. It was claimed to burn easily and rapidly without explosion, and to be less liable to freeze than ordinary dynamite.

Rexite, already mentioned, contains trinitrotoluene.

vi. *Dynamites containing Nitric Esters.*

The nitric ester almost invariably used is soluble nitrocotton.

Blasting gelatin. Owing to the tendency of nitroglycerin to exude from the dynamites containing a base of either kieselguhr or an explosive mixture, Nobel continually experimented in the direction of thickening the nitroglycerin by dissolving some substance in it; preferably an explosive. He tried guncotton as early as 1867, but it was not until accident led him, in 1875, to try collodion with the assistance of a solvent, that the problem was solved. He found that 7–8 p.c. of collodion cotton could be dissolved in nitroglycerin to form a plastic jelly which was impervious to water (Fr. Pat. 106384, 1875). Subsequently, Nobel found that warm nitroglycerin would itself dissolve the collodion cotton without the assistance of a solvent. The resulting explosive was known as 'blasting gelatin' or 'nitrogelatin.' It has been mentioned that nitroglycerin contains an excess of 3·52 p.c. of oxygen above that required for the complete combustion of the carbon and hydrogen of the nitroglycerin; this oxygen is utilised in effecting the complete combustion of the nitrocotton, itself deficient in oxygen. The composition is

consequently most powerful, and it is also proof against the action of water. This class of dynamite has now practically displaced the previous types of dynamite in England and most continental countries.

Composition.—The relative proportions of the two ingredients vary somewhat. Blasting gelatin was first experimented with on the large scale in Austria, and the usual proportion there is 7 p.c. nitrocotton to 93 p.c. nitroglycerin. The same proportions are used in Germany. In England and Switzerland, the nitrocotton varies between 5 and 10 p.c., usually about 7 p.c. In Italy 8 parts of nitrocotton are dissolved in 90 parts of nitroglycerin, with the aid of methyl alcohol.

The nitrocotton used is the so-called collodion cotton or soluble nitrocellulose, which should be as dry as possible. It should have as high a nitrogen content as is compatible with complete solubility in nitroglycerin. The nitrocotton, for this purpose, requires very special preparation, and even now the conditions are not perfectly understood for the preparation of a nitrocotton fulfilling the above requirements, and also giving a perfectly stiff and dry blasting gelatin, that will not exude nitroglycerin when stored in hot climates. A nitrocotton of the correct type is, however, essential: stiffening by the addition of more nitrocotton of a poor quality is of no value, as the gelatin resulting, though hard when first manufactured, rapidly deteriorates, and exudes nitroglycerin on storage, especially in hot climates.

Manufacture.—In the preparation of small quantities, the weighed charge of nitroglycerin is introduced into a square, jacketed copper or lead trough, heated by the circulation of hot water. When the nitroglycerin is hot, the charge of collodion cotton is gradually added, the mixture being stirred with a wooden paddle from time to time for 2 hours until the gelatinisation is complete and the jelly in the tanks is semi-transparent. The mass is then kneaded by hand until perfectly uniform. The temperature of the nitroglycerin is usually kept between 35° and 40°: occasionally, temperatures approaching 45°–50° are used, but the operation becomes very dangerous at the higher temperature, and this is only used under exceptional circumstances, when the solution of the nitrocotton is sluggish, usually due to the nitrocotton being damp.

On a larger scale, the kneading is done mechanically. The apparatus in use at Ardeer at the time is described by McRoberts in a paper read before the Society of Chemical Industry in May, 1890 (J. Soc. Chem. Ind. 1890, 267), but most factories now use the 'nitro-universal incorporator' kneading machines of Werner, Pfleiderer, and Perkins, such as are used in the manufacture of smokeless powders (*q.v.*).

The use of a solvent such as methyl alcohol does away with the necessity for heat in the process, and also renders the explosive less sensitive and less liable to freeze, but the explosive power of the product is also lowered and the addition is not usual.

The gelatin paste is finally worked into cartridges by some form of Archimedian-screw machine, the mass being too stiff for the presses used for ordinary dynamite, such as that described by McRoberts (*l.c.*), the resulting rod of gelatin being cut across by bronze knives into cylinders of the requisite length, 3–4 inches, and wrapped in parchment- or paraffined paper.

Properties.—Blasting gelatin is a translucent, elastic semi-solid of light-yellow colour and of sp.gr. 1·55 to 1·59. It does not deteriorate by submergence in water, water not separating the nitroglycerin—an advantage over kieselguhr dynamite No. 1. It freezes at low temperatures; but while some cartridges freeze readily at about 2° to 4°, others are sometimes found which are not frozen by 24 hours' exposure to the temperature of a mixture of ice and salt. If well made, blasting gelatin exudes no nitroglycerin even after repeated freezing and thawing. In the frozen state, blasting gelatin is more sensitive to shock; a rifle bullet can be fired through any number of unfrozen cartridges without exploding them, but similarly fired through frozen cartridges never fails to cause their explosion. In the frozen state it is even more sensitive than ordinary dynamite. The transmission of detonation through unfrozen blasting gelatin is much slower than through either nitroglycerin or dynamite, but the frozen gelatin cartridges appear to detonate as quickly as those of dynamite. Blasting gelatin cannot be exploded in trains in the open like dynamite, but it explodes readily when confined in boreholes, and its comparatively slow detonation makes it especially useful in blasting soft rock. Between steel and steel, blasting gelatin explodes under a blow of 25·3 foot-lbs. Soft blasting gelatin has been exploded between brass plates by a 56-lb. weight falling 12 feet, the height required when the blasting gelatin was frozen being only 1 foot. From experiments made at Ardeer, it was found that while kieselguhr dynamite No. 1 could be unfailingly exploded by a detonator containing 0·05 gram of cap mixture (70 p.c. mercury fulminate and 30 p.c. potassium chlorate), the least quantity required to detonate the best blasting gelatin is 0·2 gram; and if the latter is tough, with an extra proportion of nitrocotton (*e.g.* with 9 p.c. or 10 p.c.), it fails to detonate completely even with a 0·8 gram charge of cap composition. It is necessary, therefore, in order to get unfailing detonations with tough blasting gelatin, to use in actual mining a detonator with at least 1 gram of cap composition, or to use a dynamite primer. In small quantities, blasting gelatin burns away in the open without explosion. When gradually heated up, it explodes at about 204°; on rapid heating, it explodes at 240°. Blasting gelatin containing camphor cannot be exploded by gradual heating, but burns quickly away (Hess).

The addition of camphor (about 4 p.c.) to blasting gelatin deadens the sensitiveness of the latter to shock to a very remarkable extent. Rifle shots will not explode soft blasting gelatin containing 4 p.c. camphor at a distance of 150 paces. Berthelot attributes this effect to a certain amount of elasticity and solidity caused in the gelatin by the added camphor, on account of which the energy of the shock of the detonator, and the heat into which some of it is converted, are imparted to a much greater mass of substance than when no camphor is present,—a condition unfavourable to a sudden and local

rise of temperature. Before the introduction of 'ecrasite,' blasting gelatin containing 4 p.c. of camphor was used in Austria for military purposes as a high explosive. In Italy, 5 parts of camphor were added to 100 parts of nitrogelatin containing 8 p.c. of nitrocotton. These mixtures were so insensitive to shock that a special primer had to be used—in Austria, a mixture of nitroglycerin and nitrohydrocellulose; in Italy, guncotton.

Abel found (by the work done in expanding the bore of a lead cylinder) the intensity of action of Nobel's blasting gelatin to be about 160 when a sufficiently strong detonator was used, kieselguhr dynamite No. 1, exploded by the same detonator, being equal to 100. Abbot found the intensity of the same kind of blasting gelatin, detonated under water and referred to the same standard, to be 142. Hence it is not surprising that, although higher in price, blasting gelatin has to a large extent replaced kieselguhr dynamite.

According to Berthelot, the equation for the combustion of blasting gelatin containing 91·6 p.c. nitroglycerin and 8·4 p.c. nitrocellulose, the proportion for complete combustion is:

$$51C_3H_5(NO_3)_3+C_{24}H_{31}O_{11}(NO_3)_9 = 177CO_2+143H_2O+81N_2.$$

The heat liberated by the equivalent weight, 12,360 grams, being 19,381 cals., or 1535 cals. per kilo.

Testing: *Heat test.*—50 grains of blasting gelatin intimately mixed with 100 grains of French chalk must withstand the Abel heat test at 160° for at least 10 minutes.

Liquefaction test.—A cylinder, of equal height and diameter, exposed to a temperature of 85° to 90°F. for 144 consecutive hours, must not diminish in height more than one-fourth of its original height, nor lose the sharpness of its edges.

Exudation test.—On subjecting, three times in succession, to alternate freezing and thawing, and in the liquefaction test, no substance of a less consistency than the bulk must separate out.

Although suitable for military purposes, blasting gelatin is too violent in its effects for most mining operations, and various modifications were soon made to reduce its power. The usual way of doing this is to make a thinner gelatin and knead it into an absorbing powder. The earlier absorbents were usually a mixture of wood pulp or rye flour and either potassium or sodium nitrate. Many recent continental dynamites of this class contain ammonium nitrate, the explosives being then more powerful. The manufacture of these dynamites is essentially the same as that of blasting gelatin.

Gelatin dynamite, made by Nobel's Explosives Company, consists of thin blasting gelatin mixed with wood meal and potassium nitrate. Its composition is: gelatinised nitroglycerin, 65 p.c.; potassium nitrate, 26·25 p.c.; 8·4 p.c. wood meal; 0·35 p.c. soda. The gelatinised nitroglycerin consists of 97·5 p.c. nitroglycerin and 2·5 p.c. soluble nitrocellulose. As usual, the proportions of the constituents vary in different samples: another gelatin dynamite containing nearly 80 p.c. gelatinised nitroglycerin, of about blasting gelatin composition, 16 p.c. nitre and 4 p.c. wood pulp. As made at Ardeer, the finished explosive is of pale buff colour and is very elastic. Abel, by the lead-cylinder method, found its intensity of action, when suitably detonated, to be 127 and 123 (*mean* 125), ordinary kieselguhr dynamite being 100.

Gelignite is a weaker modification of gelatin dynamite, its composition being 60–61 p.c. nitroglycerin, 4–5 p.c. nitrocotton, 7–9 p.c. wood pulp, and about 27 p.c. potassium nitrate. An estimation by Abel of its intensity of action, suitably detonated in a lead cylinder, makes it 100, *i.e.* the same as the Ardeer kieselguhr dynamite No. 1.

Ammonia gelatin A contains 30 p.c. nitroglycerin, 3 p.c. nitrocotton, and 67 p.c. ammonium nitrate.

Ammonia gelignite contains 29·3 p.c. nitroglycerin, 0·7 p.c. nitrocotton, and 70 p.c. ammonium nitrate.

Grisoutine Favier, a French safety explosive, contains 29·1 p.c. nitroglycerin, 0·9 p.c. collodion cotton, 69·5 p.c. ammonium nitrate, and 0·5 p.c. sodium carbonate.

Antigrison contains 27 p.c. nitroglycerin, 1 p.c. nitrocotton, and 72 p.c. ammonium nitrate.

Forcite. Although the early American forcites contained unnitrated cellulose, more recent samples, such as the Belgian, contain nitrocellulose, and are simply gelatin dynamites, containing from 40 to 65 p.c. of gelatinised nitroglycerin, 4–8 p.c. nitrocotton mixed with wood meal, rye flour or tar, and usually sodium nitrate, but in some cases ammonium nitrate; 1 p.c. magnesia and sulphur are also usually present. *Forcite antigrisouteuse* contains 29·4 p.c. nitroglycerin, 0·6 p.c. nitrocotton, and 70 p.c. ammonium nitrate.

Carbogelatin contains 38·5 p.c. of nitrogelatin, 49·5 p.c. nitre, 10·5 p.c. wood meal and charcoal, and 1·5 p.c. of magnesium carbonate.

Coronite contains 38–40 p.c. nitroglycerin, 1–1·5 p.c. nitrocotton, 26–28 p.c. ammonium nitrate, 3–5 p.c. potassium nitrate, 11–14 p.c. aluminium stearate, 8–11 p.c. rye flour, 2–4 p.c. wood meal, 2·4 p.c. liquid paraffin, and 0–2·5 p.c. moisture.

Gesilit is a modern German safety explosive. No. 1 contains 30·75 p.c. nitroglycerin jelly, 5·25 p.c. dinitrotoluene, 7 p.c. sodium chloride, 18 p.c. sodium nitrate, 39 p.c. dextrin. No. 2 contains 30·75 p.c. nitroglycerin jelly, 5·25 p.c. dinitrotoluene, 22 p.c. ammonium nitrate, 21 p.c. sodium chloride, and 21 p.c. dextrin.

Fordit a similar explosive, contains 24 p.c. nitroglycerin, 1 p.c. nitrocotton, 34 p.c. nitrotoluene, 2 p.c. flour, 2 p.c. dextrin, 5 p.c. glycerin, and 32 p.c. ammonium nitrate; to this mixture is added 30 p.c. potassium chloride.

Cellite is a gelatin dynamite, with the addition of ammonium oxalate, having the composition 56–59 p.c. nitroglycerin, 2–3·5 p.c. nitro cotton, 17–21 p.c. potassium nitrate, 8–9 p.c. wood meal, 11–13 p.c. ammonium oxalate, and 0·5–1·5 p.c. moisture.

Geloxite is a similar explosive which contains 54–64 p.c. nitroglycerin, 4–5 p.c. nitrocotton, 13–22 p.c. potassium nitrate, 4–7 p.c. wood meal, containing not more than 15 p.c. and not less than 5 p.c. moisture, 12–15 p.c. ammonium

oxalate, and 1 p.c. red ochre. Ochre is sometimes added to dynamites to make them resemble ordinary dynamites in appearance.

Stowite contains 58–61 p.c. nitroglycerin, 4·5–5 p.c. nitrocotton, 18–20 p.c. potassium nitrate, 6·7 p.c. wood meal specified as in geloxite, and 11–15 p.c. ammonium oxalate. A non-waterproofed wrapper of parchment is used, and a No. 6 detonator.

The permitted composition for *Phœnix powder* is 28–31 p.c. nitroglycerin, 0–1 p.c. nitrocotton, 30–34 p.c. potassium nitrate, 33–37 p.c. wood meal, and 2·6 p.c. moisture.

Safety dynamite contains 24 p.c. nitroglycerin, 1 p.c. nitrocotton, and 75 p.c. ammonium nitrate.

The *wood pulp*, so frequently used as an ingredient in these dynamites, is made from logs usually of pine wood, but occasionally from other woods. The logs are freed from bark and sawn into boards; the boards, free from knots, broken by a machine into small pieces and then crushed between rollers. Where available in sufficient quantity, shavings are used. The powder is boiled under pressure with a solution of sodium bisulphite for 10 to 12 hours. The pulp is then washed and dried. The pulp must not be exposed to acid vapours or overheated in drying, and should all pass through a sieve of 50 meshes to the inch.

The use of non-fermentable *starch* was proposed by Kynoch (Eng. Pat. 22966, 1901) as a substitute for wood meal, in order to reduce the bulk of the explosive.

Cocoanut fibre has been suggested by Gonsalves (Eng. Pat. 4968, 1905) as an absorbent for this class of dynamite, and it is claimed that it prevents the freezing of the nitroglycerin.

Guncotton dynamite. In 1867 mixtures of nitroglycerin with pulped guncotton, which, unlike collodion cotton, does not dissolve in and gelatinise nitroglycerin, were proposed by Abel and Trauzl. Abel's mixture was called *glyoxiline*, and was prepared by soaking guncotton, with or without nitre, in nitroglycerin.

Trauzl's dynamite consisted of 75 p.c. nitroglycerin, 25 p.c. guncotton, and 2 pts. charcoal to every 100 of mixture. In 1868 Schultze proposed a mixture of nitrated wood cellulose soaked in nitroglycerin under the name of '*dualine.*'

These explosives, like most other dynamites, have been superseded by the gelatin dynamite class.

Freezing of dynamites.—The comparatively high freezing-point of nitroglycerin, and the difficulty in thawing, is a great objection to the use of nitroglycerin explosives. Numerous attempts have been made to overcome the difficulty by lowering the freezing-point, by suitable additions, but with very limited success. The addition of nitrohydrocarbons such as nitrobenzene was tried by Nobel and Guttmann, but they found that so large a quantity was required to produce any sensible reduction of the freezing-point, that the power and sensitiveness of the explosive were seriously reduced. The addition of nitrobenzene had been previously patented in Sweden by Rudberg in 1866, and von Dahmen in Austria patented a process for nitrating glycerine mixed with a small percentage of nitrobenzene. Dinitrotoluene was found more efficient, and its use was patented by the Société des Poudres, &c. Dynamites, of Arendonck in 1903 (Eng. Pat. 14827, 1903) and a mixture of solid di- and trinitrotoluene was suggested by Johnson (Eng. Pat. 25797, 1904).

Wohl, in 1890, had suggested the use of mono- and dinitroglycerin for reducing the freezing-point of nitroglycerin, and in 1904 Mikolajczak patented the use of dinitroglycerin (Eng. Pat. 8041, 1904); but mono- and dinitroglycerin are hygroscopic, soluble in water, and expensive, and moreover Will has shown that their addition is not very effective.

The Westfälisch-Anhaltische Sprengstoff-Gesellschaft, in 1906, patented the use of nitrochlorhydrins and subsequently the nitropolyglycerins (Eng. Pat. 4057 and 6314, 1906). Vender proposed dinitroacetin and dinitroformin (Eng. Pat. 9791, 1906) and Escales (Eng. Pat. 2117, 1907) used a nitrated complex mixture of mono- and di-chlorhydrin, di- and tri-glycerin and the chlorhydrins of these bodies.

The subject of the lowering of the freezing-point of nitroglycerin has been investigated by Nauckhoff (Zeitsch. angew. Chem. 1905, 11, 53). He showed that the freezing-point of a nitroglycerin explosive can be calculated from its composition, by means of Raoult's formula, and that the value of a substance for depressing the freezing-point of nitroglycerin depended on its molecular weight and not on its own freezing-point. He pointed out, further, that the resistance to freezing depended, not only on the true freezing-point of the mixture, but also on its property of undergoing cooling below its freezing-point without solidifying, and found that the property was best shown in more plastic explosives.

Nitrocelluloses.

Braconnot, in 1832, observed that starch, woody fibre, and other similar substances, are converted by the action of strong nitric acid into a combustible product, which he called *xyloïdine*. Pelouze, in 1838, found that starch treated with strong nitric acid increased in weight; and that paper, cotton, and linen, immersed in nitric acid of 1·5 sp.gr., become easily combustible. Schönbein, towards the end of 1845, announced the discovery of a new explosive substance, which he subsequently stated to have been obtained by treating cotton with a mixture of nitric and sulphuric acids. Böttger, in August 1846, found out the method of making guncotton, which Schönbein was keeping secret. The two chemists jointly submitted their discovery to the Germanic Confederation, but reserved the publication of their method of preparing guncotton. Several chemists having in 1847 independently discovered the method of preparing guncotton by means of a mixture of nitric and sulphuric acids, Schönbein and Böttger then stated this to be their process. The manufacture of guncotton was undertaken in England, France, and Russia; but the earlier attempts at manufacture were not satisfactory, the importance of purifying the cotton from fatty matter, and of washing the guncotton thoroughly free from acid, not having at first been sufficiently felt to be essential to obtaining a safe and stable guncotton.

Von Lenk, in Austria, between 1849 and 1852, made great improvements in the manufacture of guncotton; and in 1853 a factory was erected under his direction at Hirtenberg, near Vienna, in which (and at Reny in Vienna) the manufacture was continued until 1865, when the manufacture and use of guncotton were officially put a stop to in consequence of the explosion of two magazines. Von Lenk used the cotton in the form of yarn; his principal improvements were the purification of the cotton from oily and other matters by boiling with caustic alkali, the nitration of the cotton in separate small charges, the dividing the operation of nitration into two stages: a short immersion (of some minutes) of the cotton in the mixed acids, the removal of the cotton with a sufficiency of absorbed acids, and allowing a long time (24 to 48 hours) for the completion of the nitration, also the careful washing of the guncotton to remove free acid. To remove acid, the guncotton after its nitration was whirled in a centrifugal machine, washed in copper drums with a large quantity of water, then placed in boxes in running water for three to six weeks, after which it was treated with a hot weak solution of potash, and again water-washed.

Von Lenk's guncotton was used in the form of yarn.

Abel, adopting Von Lenk's method of nitrating the cotton, made very important improvements in the processes of manufacture. He introduced the use of cleaned cotton waste, and by converting the guncotton into pulp so facilitated the washing that it could be effected in two or three days instead of in six or more weeks as in Von Lenk's process. Further, by compressing the finished pulp by hydraulic pressure, he rendered it possible to detonate it in an unconfined state. The pulping and compressing of the guncotton were introduced in 1865.

Composition.—Guncotton, when the process of manufacture has been well conducted, and when the strongest acids have been used, has the composition of trinitrocellulose $C_6H_7O_2(NO_2)_3$, when cellulose is $C_6H_{10}O_5$.

This composition was deduced by Abel from the results of a large number of analyses (in which C, H, and N were determined) of guncotton of Waltham Abbey make. The mean numbers given by these analyses of the dry guncotton, ash deducted, are given below, and are compared with the percentages calculated for trinitrocellulose:

	Mean of analyses	$C_6H_7O_2(NO_2)_3$
Carbon . .	24·57	24·24
Hydrogen . .	2·46	2·36
Nitrogen . .	13·83	14·14
Oxygen . .	59·14	59·26

The percentage of carbon is slightly raised, and that of nitrogen slightly depressed, by the presence in the guncotton of a few per cents of less highly nitrated cellulose than the trinitro derivative, and soluble in ether alcohol (Abel, Phil. Trans. 1866, 156, 269–308).

The formation of trinitrocellulose from cellulose is represented by the equation:

$$C_6H_{10}O_5+3HNO_3=C_6H_7O_2(NO_2)_3+3H_2O,$$

from which 100 parts by weight of cotton should give 183·3 parts by weight of trinitrocotton.

Abel (*l.c.*), as the result of a large number of experiments, found a maximum increase of 82·6 p.c., which is a close approach to the theoretical 83·3 p.c., and confirms Hadow's previously observed increase of 81·3 p.c.

Soluble nitrocellulose.—Abel found that the part of guncotton soluble in a mixture of alcohol and ether is a less highly nitrated compound than his trinitrocellulose; it approaches in composition dinitrocellulose (Proc. Roy. Soc. 1866). In a further series of experiments, in 1868, Abel examined the influence on the nitration of the cotton of an addition of water to the acids. Using mixtures of 60 lbs. nitric acid, sp.gr. 1·42 and 65½ lbs. sulphuric acid, sp.gr. 1·835, without addition of water, and also with the addition of 3 lbs. of water, he obtained nitrocottons, which, after reprecipitation from solution in ether-alcohol, had percentages of carbon 28·56 and 28·13 respectively: the calculated percentage in dinitrocellulose $C_6H_8O_3(NO_3)_2$ being 28·57.

For a long time, nitrocelluloses were divided into two kinds only—trinitrocellulose, guncotton, or insoluble nitrocellulose, and dinitrocellulose, collodion cotton, or soluble nitrocellulose; but it was clearly shown in the cordite case, Nobel *v.* Anderson, 1894, that there are certainly more than two cellulose nitrates, and, further, that the solubility of the nitrocellulose is not invariably related to the degree of nitration, but that soluble nitrocellulose can be prepared containing almost as much nitrogen as guncotton.

Roscoe prepared, for example, a soluble nitrocellulose containing 12·73 p.c. of nitrogen, and an insoluble nitrocellulose with 12·83 p.c. of nitrocellulose.

Eder, as he was able to prepare nitrocottons in which the percentage of nitrogen is between those corresponding to the above tri- and dinitrocellulose, doubled Abel's formulæ, and claimed to have prepared the following five varieties of nitrocellulose:—

	P.c. of nitrogen
$C_{12}H_{14}O_4(NO_3)_6$ Hexa-nitrocellulose, containing	14·14
$C_{12}H_{15}O_5(NO_3)_5$ Penta- „ „	12·75
$C_{12}H_{16}O_6(NO_3)_4$ Tetra- „ „	11·11
$C_{12}H_{17}O_7(NO_3)_3$ Tri- „ „	9·15
$C_{12}H_{18}O_8(NO_3)_2$ Di- „ „	6·76

His hexanitrocellulose only was insoluble in ether-alcohol, and is ordinary guncotton.

Vieille (Compt. rend. 1882, 132) prepared nitrocottons under the most varying conditions, and stated that the nitration of cellulose, which he assumed to be $C_{24}H_{40}O_{20}$, took place in eight stages, the products being:

	P.c. of nitrogen
$C_{24}H_{29}O_9(NO_3)_{11}$ Endeca-nitrocellulose, containing	13·50
$C_{24}H_{30}O_{10}(NO_3)_{10}$ Deca- „ „	12·78
$C_{24}H_{31}O_{11}(NO_3)_9$ Ennea- „ „	11·98
$C_{24}H_{32}O_{12}(NO_3)_8$ Octo- „ „	11·13
$C_{24}H_{33}O_{13}(NO_3)_7$ Hepta- „ „	10·19

	P.c. of nitrogen
$C_{24}H_{34}O_{14}(NO_3)_6$ Hexa-nitrocellulose, containing	9·17
$C_{24}H_{35}O_{15}(NO_3)_5$ Penta- " "	8·04
$C_{24}H_{36}O_{16}(NO_3)_4$ Tetra- " "	6·77

Of these, the endeca- and deca-nitrocelluloses were insoluble in ether-alcohol.

Berthelot, following Vieille, regards guncotton as $C_{24}H_{29}(NO_2)_{11}O_{20}$ (mol. wt. 1143).

He finds the heat evolved by the nitration of cotton in accordance with the equation:

$$C_{24}H_{40}O_{20}+11HNO_3=C_{24}H_{29}O_9(NO_3)_{11}+11H_2O$$

to be $11 \times 11{\cdot}4=125{\cdot}4$ kgm.-degrees per 1·143 kgm. of guncotton formed. The heat of formation of endecanitrocellulose from its elements (diamond carbon, gaseous hydrogen, oxygen, and nitrogen), Berthelot finds to be +624 kgm.-degrees per 1·143 kgm., or +546 kgm.-degrees per 1 kgm.

These formulæ of Vieille were soon contested. Guttmann claimed to have made guncotton on the large scale containing 13·65 p.c. nitrogen; Hoitsema (Zeitsch. angew. Chem. 1898, 173) obtained a product containing 13·9 p.c. nitrogen; and Lunge (J. Amer. Chem. Soc. 1901, 527), with an acid mixture containing 63·35 p.c. H_2SO_4, 25·31 p.c. HNO_3, and 11:34 p.c. water, prepared nitrocellulose with 13·92 p.c. nitrogen, corresponding very closely to

$$C_{24}H_{28}O_8(NO_3)_{12}$$

dodecanitrocellulose, containing 14·16 p.c. nitrogen; but this substance, like that with a similar nitrogen content, obtained by nitrating cotton with a mixture of equal parts of nitrogen pentoxide and phosphorus pentoxide (*cp.* Hoitsema, *l.c.*), was not stable, and on keeping, the nitrogen content fell to 13·5 p.c., at which point it remained constant. In a further series of experiments, Lunge found that when all water was eliminated by adding fuming sulphuric acid, the p.c. of nitrogen was not altered, even when such varying ratios of H_2SO_4 to HNO_3 as 3·3 : 1 to 2 : 1 were used.

Lunge found that with nitrocellulose of less than 10 p.c. nitrogen, the solubility rapidly decreased and confirmed Vieille's results that below $C_{24}H_{32}O_{14}(NO_3)_6$ the products are insoluble. He also found that with dilute acids, the products contained oxycellulose, the proportion of the latter gradually increasing until eventually it was the only product. Saposchnikoff (Zeitsch. ges. Schiess- u. Sprengstoffwesen, 1906, 453) shows a close relationship between the vapour pressure of the nitric acid in the mixed acids and the nitrogen content of the products.

Berl and Klaye (Zeitsch. ges. Schiess- u. Sprengstoffwesen, 1907, 403) show that the process of nitration of cellulose is a reversible reaction, represented by the equation:

$$C_{24}H_{40}O_{20}+nHNO_3 \rightleftarrows C_{24}H_{40-n}O_{20-n}(NO_3)_n+nH_2O$$

and that after a certain maximum substitution is obtained, about 13·5 p.c. nitrogen, the sulphuric acid of the nitrating mixture acts as a hydrolysing agent.

Berl and Smith (Ber. 1907, 1903) prepared esters of cellulose in order to show the number of free hydroxyl-groups in the cellulose molecule. They found it impossible to introduce more than twelve substituted groups into the cellulose molecule of $C_{24}H_{40}O_{20}$, which agrees with the results of Ost (Zeitsch. angew. Chem. 1906, 992), and Green and Perkin (Chem. Soc. Trans. 1906, 811), but did not succeed in obtaining a nitrocellulose with a higher nitrogen content than 13·50 p.c.

Any preparation of nitrocellulose is a mixture of definite nitrates, the nature of which depends on the nature of the nitrating mixture, the time and temperature of nitration, and the method of purification.

A large excess of mixed acids is necessary in the nitration of cellulose, partly because of the bulk of the latter, but also to obtain products of constant composition. The acid mixture is diluted during nitration, both by the formation of water and by the abstraction of nitric acid during the nitration, and both these factors tend to lower the nitrogen content of the product, unless the bulk of the mixed acids is large. The speed of nitration is diminished with increase in the quantity of sulphuric acid.

As far as explosives are concerned, only two forms of nitrocellulose need be distinguished: guncotton or insoluble nitrocotton, and collodion or soluble nitrocotton. When the soluble nitrocellulose is referred to in this article without qualification, solubility in ether-alcohol is always inferred.

Nitrohydrocellulose and *nitrooxycellulose.* Hydrocellulose $C_{12}H_{22}O_{11}$, cellulose being $C_{12}H_{20}O_{10}$, is prepared by soaking cotton for 12 hours in sulphuric acid of 1·45 sp.gr. at 15°, or for 24 hours in hydrochloric acid of 1·17 sp.gr. (Girard). Cross and Bevan prepared oxycellulose by boiling cellulose with nitric acid, and found its composition to be $C_{18}H_{26}O_{16}$. The nitro body obtained from it by nitration with a mixture of equal volumes of strong sulphuric and nitric acids, contained 6·48 p.c. nitrogen, and was given the formula:

$$C_{18}H_{23}O_{13}(NO_3)_3$$

(Chem. Soc. Trans. 1883, 22).

Vignon (Compt. rend. 1898, 136) found that oxycellulose, prepared by the action of a mixture of hydrochloric acid and potassium chlorate on cellulose, had a constant composition represented by $3C_6H_{10}O_5+C_6H_{10}O_6=C_{24}H_{40}O_{21}$.

Both these bodies, which may be formed in the nitration of cellulose, can be themselves nitrated. Hydrocellulose nitrates more slowly than cellulose, giving stable but rather sensitive products, and oxycellulose gives an unstable nitro product. Amorphous nitro products of oxy- and hydro-cellulose can be prepared by treating cellulose with sulphuric acid containing a little nitric acid at a low temperature until the mass becomes pasty, then nitrating and purifying as usual. Vignon (*l.c.*) found that nitrocellulose, prepared according to Lunge's formula for highest nitration, gave on determination of their C, H, and N, results agreeing with the formula

$$3C_6H_7O_2(NO_3)_3+C_6H_7O_3(NO_3)_3 = C_{24}H_{28}O_9(NO_3)_{12}.$$

He concludes from this that this so-called nitrocellulose is an oxycellulose derivative, and attributes discrepancies in the results of others to the fact that the nitrogen only is estimated.

Later (Compt. rend. 1900, 509), Vignon determined the copper-reducing powers of nitrated cellulose and nitrooxycellulose, and found them identical and independent of the degree of nitration, and as oxycellulose reduces cupric potash solution, whilst cellulose and hydrocellulose do not, concludes that, on the nitration of cellulose, oxycellulose is formed, and that the product is really nitroxycellulose.

Guncotton.

Manufacture.—The process of manufacture of guncotton, with some modification in detail, is still the process of Von Lenk, as modified and improved by Abel.

Prime materials: Cellulose.—Although many forms of fibrous cellulose materials have been from time to time tried, practically the only form of cellulose used for the manufacture of guncotton is the cotton waste from spinning mills and other sources. The quality of the waste from different sources varies considerably, and it is important that it should be as pure as possible in order to obtain a good yield of pure guncotton. The previous treatment of the cellulose has been shown by Piest (Zeitsch. angew. Chem. 1909, 215) to have considerable influence on the preparation and properties of nitrocellulose. The product from strongly bleached or mercerised cotton has a lower nitrogen content and higher solubility, and is more difficult to stabilise than that from ordinary cotton.

Formerly the waste was purified by boiling with a 2 p.c. solution of sodium carbonate and subsequent washing, but the modern purification process is more complicated. The waste is first of all de-greased by means of a solvent, then boiled with caustic soda, bleached with bleaching powder or calcium sulphide, washed, neutralised with sulphuric or hydrochloric acid, washed again, and finally dried. The resultant cotton is nearly pure cellulose, with little or no altered, oxy-, or hydro-cellulose. It should contain no chloride, sulphate, or sulphide of lime, and be free from dust. It contains less than 0·3 p.c. of fatty matter, but usually the uncarded waste used in the manufacture of guncotton contains a considerable quantity of impurities, such as wood, cane, string, coloured threads, metal, indiarubber, &c. These impurities are removed as far as possible by handpicking, and the cotton is then passed through a 'teasing machine' or 'willow,' a combination of drums armed with sharp-pointed teeth, which tear the threads apart and open out the knots and lumps. The cotton is picked over again as it leaves the machine, dried on an endless band in a current of hot air, which is often first dried over sulphuric acid or calcium chloride, and then weighed out in charges, placed in tightly closed receptacles, and allowed to cool.

Mixed acids.—The acids used in the manufacture of guncotton are of a high degree of purity, free from solids, and of maximum concentration. The proportions of acid employed until recently were those used by Von Lenk, namely, 1 part of nitric acid of 1·5 sp.gr., containing not more than 1·5 p.c. of nitrous acid, and 3 parts of sulphuric acid of 1·84–1·85 sp.gr. In other words, the nitric acid contained at least 93 p.c. of monohydrate, and the sulphuric acid 95–96 p.c. of monohydrate. The more modern mixtures vary slightly in composition according to the method of nitration, and are given under these various methods.

The experiments of Lunge (*l.c.*) have shown that it is not necessary to have acid mixtures containing only a few per cents of water, and that with acids of the proportion of $3H_2SO_4$ to $1HNO_3$, it is possible to work with as much as 12 p.c. of water. Not only is the acid mixture cheaper, but Lunge agrees with Will that the nitrocellulose manufactured with the more dilute mixtures is more stable than when produced by highly concentrated acids.

Most explosive factories have plant for the manufacture of the nitric acid, and for the recovery of waste acids, the latter being revivified and used again. The acids are mixed in large quantities, analysed, and the composition adjusted to that required, by the addition of strong acids in the requisite proportions. Nordhausen sulphuric acid is now in common use for decreasing the proportion of water.

Mechanical mixing of the acids was at one time generally practised, but it was subsequently found that a perfect admixture was obtained by running the sulphuric into the nitric acid. However, the acids are now frequently mixed by means of compressed air, means being adopted to condense the nitric acid vapours.

The acids are stored and transferred from place to place as already described in the manufacture of nitroglycerin.

Nitration.—Lunge (*l.c.*) has shown that the speed of nitration increases rapidly, but the yield falls, with rise in temperature, the nitrogen content of the product varying but slightly. He concludes that the ordinary method of nitrating at a temperature not exceeding 25° is correct for obtaining maximum nitration and maximum yield. An outline of the nitration process used by Von Lenk has already been given.

Abel's nitration process, as formerly carried out at the Royal Gunpowder Factory, Waltham Abbey, and still used in many factories in England and abroad, is shortly as follows:—

The mixed acids are drawn off from the store tanks into a tank in connection with the dipping pans. These latter are of cast iron; each holds about 220 lbs. of mixed acids, and is provided with a grating. The charge of 1¼ lb. of cotton is then, by small portions, quickly immersed in the mixed acids. After an immersion of 5 or 6 minutes, the cotton is removed to the grating, and squeezed by means of a lever with a plate at one end. The charge, which with the acid now weighs about 15 lbs., is placed in a closely covered earthen pot, in which it is allowed to remain for at least 24 hours, during which time the pots are placed in constantly flowing cold water. By this prolonged action, the nitration of the cotton is completed; the cooling is needed to prevent complete decomposition of the product by oxidation, and the maintenance of a low temperature is said to be favourable to the production of guncotton with a low percentage of soluble nitrocotton.

Much of the acids is then removed from the guncotton by means of the centrifugal machine made entirely of iron, the contents of six pots being whirled for 10 minutes at the rate of about

1200 revolutions per minute. The guncotton is then, in small quantities, plunged by means of an iron fork beneath a cascade of water, which carries it into a large cistern, where it is kept stirred by a paddle wheel, and is washed by fresh water continually admitted, until the guncotton has no perceptible acid taste, when it is whirled in a centrifugal machine, after which it is ready for the boiling process. The yield by this process is about 164 p.c. of the cotton nitrated.

In the Abel process, there is considerable wear and tear of the plant, and there is occasionally loss of guncotton owing to decomposition taking place in the digesting pots. Moreover, there is a considerable expenditure of labour and power involved, and improvements have been made to overcome these disadvantages.

Direct-dipping process.—In the direct-dipping process, as used at Nobel's factory at Ardeer, the operation of nitration is completed in one stage. The nitration is carried out in a series of iron pots, termed 'dippers,' standing in cold water contained in long cooling tanks, the pots being closed by covers which lead away the acid fumes to exhaust pipes. Each dipper is fed with 127 lbs. of mixed acid, the temperature of the acid is adjusted to 15°, and the charge of 4½ lbs. of cotton gradually added, the temperature rising to 25°. The nitration is allowed to proceed for from 8 to 24 hours, according to the composition of the nitrating mixture, the temperature gradually falling to 20°. The mixed acid for a 12 hours' immersion is 75 p.c. sulphuric acid, 15·75 p.c. nitric acid (monohydrate) and 9·25 p.c. water. The more rapid the nitration, the higher the proportion of nitric acid and the less the proportion of water used.

When the nitration is complete, the contents of the dippers are transferred to centrifugals, and the waste acids whirled out. The guncotton is then treated as in the Abel process. The yield by this process is about 159 p.c. of the cotton nitrated.

Centrifugal process.—In this process, largely used on the Continent, the nitration is carried on in a perforated iron basket, rotating in an outer iron casing, the centrifugal being covered with a lid fitted with a fume pipe. The nitrating acid is run in and the cotton charge of 17½ lbs., or in a large-sized centrifugal 26½ lbs., gradually added whilst the basket is slowly rotating. The effect of the rotation is to produce better contact between the cotton and acids, and the nitration only occupies from 30 minutes to an hour. When the nitration is complete, the bulk of the waste acid is drawn off, and the centrifugal set rotating rapidly, the guncotton being afterwards "pre-washed" as usual.

In this centrifugal without acid circulation, the nitrating acid is about ten times the weight of the cotton charge, the composition of the acid being about 23·15 p.c. HNO_3, 69·35 p.c. H_2SO_4, and 7·5 p.c. water.

The usual forms of nitrating centrifugal used are those of Messrs. Selwig and Lange, of Brunswick, who, in 1904, patented an improved form in which the acid is caused to circulate continuously through the material by means of a pump, for the purpose of producing a more uniform nitration and avoiding local centres of heating.

Guttmann suggested the use of aluminium baskets, but, although more acid-resisting than the usual cast-iron baskets, the metal was found to be too soft and to get out of shape. The yield by this process of nitration is 160 p.c. of the cotton nitrated.

Displacement process.—In 1903 (Eng. Pat. 8278) J. M. and W. T. Thomson, of the Royal Gunpowder Factory, patented a new method for the nitration of cotton which has been used at Waltham Abbey since 1905. The apparatus consists of sets of four circular earthenware pans, 3 feet 6 inches in diameter and 10 inches deep at the side, with a slight fall towards the centre of the bottom. They are furnished with perforated false bottoms, and are connected at their lowest points with a lead pipe provided with a stopcock, which leads to the acid supply pipes, the waste acid pipe and the waste water pipe. The pans are covered by aluminium hoods with fume pipes. The process is as follows: 650 lbs. of nitrating acid of the composition 70·5 p.c. H_2SO_4, 21 p.c. HNO_3, 0·6 p.c. nitrous acid, and 7·9 p.c. water, adjusted to a temperature of from 10° to 15°, is run into one of the pans, and the charge of 20 lbs. of cotton is gradually added and pushed below the surface of the acid. The contents are then covered with a perforated plate in sections, a flow of water carefully run over the plate, and the fume hoods removed. When nitration is complete, after about 2½ hours, water is slowly run over the surface of the acids in the nitrating vessel, and by opening the stopcock the acids are allowed to be displaced at an equal rate. Most of the waste acid is allowed to flow back to the store tanks, where it is revivified with strong nitric acid and Nordhausen sulphuric acids, the remaining weaker acid being denitrated and concentrated. When the whole of the acid is displaced, the water is allowed to run off through the guncotton, and the latter, after draining, is apparently neutral, and is ready for the boiling process. The yield in this process is about 170 p.c. of the cotton nitrated, and the product is more evenly nitrated than by the Abel process.

De Brailles (Fr. Pat. 364349, 1906) has patented a system of concentrating the acids in the nitrator by electrolysis. Voigt (U.S. Pat. 855869, 1907) disintegrates the cotton fibre before nitration by immersing in sulphuric acid with only 3 p.c. nitric acid at 2°, and ultimately obtains the nitrocellulose in the form of a fine powder.

Boiling.—After the nitration and preliminary washing, the guncotton is 'boiled' in order to purify and stabilise it. The impurities removed are the last traces of free acid and unstable products of the nitration. Amongst the latter are ill-defined unstable bodies, such as nitrosaccharoses, formed by the action of the nitrating acids on the impurities in the cotton, and cellulose esters, other than the higher nitrates, such as the sulphuric esters, mixed nitrosulphuric esters, and possibly nitrous esters and low nitric esters. The possibility of the presence of sulphuric esters in unstabilised nitro-cotton was pointed out by Cross and Bevan in 1901; and Hake and Bell examined their mode of formation and influence on the stability of nitrocellulose (J. Soc. Chem. Ind. 1905, 374;

1909, 457). Hake and Bell conclude that mixed sulphuric esters exist in all products of the nitration of cellulose, and that they are formed owing to delayed nitration, caused by partial solution or gelatinisation of the cellulose by sulphuric acid and subsequent fixation by nitric acid. The amount of sulphuric acid normally fixed during nitration is about 1 p.c., but this is reduced during the stabilisation to about 0·1 to 0·3 p.c.

Will found that the stability of nitrocellulose was increased by increasing the amount of water in the nitrating mixture, whilst insufficient washing lowers the stability, and that the stability decreases with increase of nitrogen content. The degree of comminution of the cotton was found to have but little effect on the stability, which was contrary to the opinion generally held at the time as to the value of the pulping process in effectively stabilising guncotton, and he also found that there is a limit to the boiling process, beyond which there is no increase in the stability.

Berthelot, in 1900, pointed out the possibility of the formation of nitrous esters, and Lunge and Bebie have examined their influence on the stability of nitrocellulose (Zeitsch. angew. Chem. 1901, 539).

In the old Abel process, the guncotton received two boilings by means of steam in wooden vats, the water being separated by centrifugal machines after each boiling. In many factories, a 2 p.c. solution of soda was used in order to reduce the time of boiling, the function of the alkali being not so much to neutralise residual traces of acid as to decompose and dissolve unstable impurities; but this was found to decompose the guncotton, and was abandoned in England, and water only used. The boiling was subsequently extended; several boilings were used, and the boiling process sometimes lasted 4 or 5 days in all. At Waltham Abbey, previous to the introduction of the displacement process, a system of twelve short boilings of gradually increased duration was practised.

Robertson (J. Soc. Chem. Ind. 1906, 624), as the result of numerous experiments at Waltham Abbey, in 1905, with displacement guncotton, found that boiling in dilute acid at the beginning of the process is superior to an alkaline treatment for the elimination of impurities. He found that good results were obtained when the wash water contained acid equal to 1 p.c. of H_2SO_4 on the guncotton present, and sufficient should be left in the guncotton to give this result. At Waltham, the water is hard and the dissolved chalk makes the water sufficiently alkaline for the subsequent boiling. As a result of Robertson's experiments, the present Waltham Abbey system of boiling is a series of two 12, five 4, and three 2 hours' boiling, with a cold-water washing after each of the first two boilings.

Too prolonged boiling causes loss of nitrogen and increase in the percentage of the lower nitrates constituting soluble nitrocellulose (Bruley, Mem. des Poudres et Salpêtres, 1895–6, 131).

Many suggestions have been made for improving on the boiling process for stabilising guncotton. Luck and Cross claim that, for the production of nitrocellulose for industrial purposes, washing with dilute acetone stabilises more quickly than the ordinary boiling process. Haddan (Eng. Pat. 5830, 1900) claims that heating for 6 hours with water under pressure at 135° is equivalent to 100 hours' ordinary boiling. Du Pont (U.S. Pat. 724932, 1903) suggests agitating with water and air under pressure and suddenly releasing the pressure; and Selwig and Lunge (Fr. Pat. 327803, 1902) introduce steam into the pulped guncotton whilst it is being rotated in centrifugals, and claim that stabilisation is very rapidly effected in this way.

Pulping.—The next operation to which the guncotton is subjected is that of pulping, which is done by means of a slight modification of the machine like that known as 'the beater,' which is used in paper making for pulping rags. The pulping takes 5 hours, and has to be so conducted that the pulp is not too coarse nor too fine. The reduction in the length of the fibres allows of the last traces of acid being washed out of the fibre canals. Guttmann first introduced live steam into beaters, and so enabled the previous boiling to be considerably reduced. In modern beaters, the water is constantly renewed during the pulping, and the pulp is frequently pumped over a strainer or 'knotter,' to remove large pieces. After pulping, mechanical impurities are removed from the guncotton, usually by passing the guncotton suspended in a large bulk of water, through long troughs in which the grit settles, and is caught in traps, and over electromagnets to remove any particles of iron.

Poaching.—The guncotton is then led into large oval tanks called 'poachers,' each holding about 10 cwts. of guncotton and 1100 gallons of water, in which a paddle wheel rotates and keeps the pulp in agitation. The pulp is washed at least three times, being allowed to settle, and the washing water containing suspended impurities removed by a skimmer between each operation.

Moulding and pressing.—The treatment in the poacher serves not only to complete the washing, but also to thoroughly mix the products of a large number of nitrating operations, thus securing uniformity of product. If the pulp passes the heat test after this treatment, it receives an addition of alkali sufficient to leave in the finished guncotton from 1 p.c. to 2 p.c. alkaline matter, calculated as $CaCO_3$. By means of vacuum pressure, the pulp is then drawn up into the 'stuff chest,' a cylindrical iron tank, large enough to hold the contents of one poacher, and in which revolving arms keep the pulp uniformly mixed with the water, so that it can be drawn off as required to be moulded into cylinders and slabs. The requisite quantity of suspended pulp is found by means of small measuring tanks, and is run into moulds of the required size and shape. The moulds have bottoms of fine wire gauze, through which a large part of the water is sucked from the pulp by evacuation. Hydraulic pressure of about 34 lbs. per square inch is then applied, which squeezes out some of the water, and gives sufficient consistency to the guncotton to allow of careful handling. The mass is then removed to the press-house, and there subjected to powerful hydraulic pressure of about 5 to 6 tons per square inch.

Those slabs and cylinders which are to serve as primers (*i.e.* which are dried and receive the fulminate charge, and by their own detonation cause that of the moist guncotton) have holes bored in them while moist, to receive the tube of the detonator; and the slabs of wet guncotton may be sawn, or turned on a lathe to any required shape. Primers are dried at a low temperature and usually waterproofed by dipping momentarily in acetone or molten paraffin. No alkali is added to guncotton when it is to be used for the manufacture of smokeless powders.

Hollings (Eng. Pat. 23449, 1899) has patented a process of compression whereby large blocks of guncotton, such as are required as a charge for large shells and torpedoes, can be made in one piece of uniform density.

Testing: Moisture is best determined by placing the sample over sulphuric acid until it is of a constant weight.

Ash.—2 grams are heated with about 10 grams of paraffin wax, added as a restrainer, first on a water-bath till the guncotton has soaked up the wax, then gently over a flame until the mass inflames. The source of heat is then removed, and when the flame dies out the residual carbon is burned off as usual. The ash is recarbonated.

Alkalinity.—10 grams are well shaken with an excess of decinormal hydrochloric acid, allowed to settle, and the excess of acid determined in an aliquot portion of the clear supernatant fluid with standard alkali.

Soluble nitrocellulose.—5 grams of the sample are well shaken for some time in a stoppered cylinder with 200 c.c. of a mixture of 2 parts of ether and 1 part of alcohol, of 0·83 sp.gr., and allowed to settle. An aliquot part of the clear solution is drawn off, carefully evaporated in a platinum dish, and the residue dried at a temperature not above 50°.

Unconverted cotton.—5 grams are well shaken for some time in a conical flask with a large bulk of acetone, and allowed to settle. The clear liquid is decanted off, the residue diluted with acetone, filtered on a tared paper, washed, and dried. The ash is then determined and deducted. Boiling with a solution of sodium sulphide is frequently used instead of solution in acetone.

Nitrogen is determined by nitrometer (with 100 c.c. bulb and graduated to 150 c.c.), 0·5–0·6 gram is dissolved in about 5 c.c. of 96 p.c. strong sulphuric acid in the cold, washed into the nitrometer with a further 10 c.c. of acid, &c.

Heat test.—The dried guncotton should withstand the Abel heat test (*see Stability tests*) at 76·6°C. (170°F.) for at least 10 minutes.

Properties.—Guncotton is an odourless, tasteless, and neutral solid, having an absolute (*i.e.* when freed from air) specific gravity of 1·66 at 15·6°. The apparent specific gravity (*i.e.* with the included air) of dry compressed Waltham Abbey guncotton at 15·6° is about 1 or a little higher than 1; even after very considerable pressure, a density higher than 1·4 cannot be obtained. When dry, guncotton is readily electrified by friction.

Guncotton retains the structure of the unnitrated cotton. Under polarised light, nitrocotton exhibits colours which both Chardonnet and Liebschütz state are determined by the nitrogen content, but De Mosenthal and Lunge find that Chardonnet's colours are not always confirmed, the colour depending not only on the nitrogen content, but also on the method of preparation. Lunge, however, states that blue colours are characteristic of nitrocellulose containing upwards of 12·75 p.c. nitrogen. De Mosenthal gives the refraction, μ_D, of guncotton, of 13·5 p.c. nitrogen, as 1·5059, and confirms Vignon in his statement that guncotton is dextro-rotatory.

Guncotton is insoluble in hot and cold water, alcohol, ether, glacial acetic acid, and (except the collodion cotton content), in a mixture of alcohol and ether. It is also insoluble in nitroglycerin. It is readily soluble in acetone, ethyl acetate, amyl acetate, nitrobenzene, &c.

Guncotton is not attacked by dilute acids, but it slowly dissolves in strong sulphuric acid with the formation of cellulose sulphate and liberation of nitric acid. Strong nitric acid violently oxidises, and may inflame, guncotton. Dilute alkalis, especially ammonia, and alkaline carbonates, decompose guncotton slowly, especially when warm. Even chalk influences guncotton unfavourably, but it is the least unsatisfactory of the neutralising agents added to guncotton, and quantities up to 2 p.c. have no appreciable effect on the stable life of a wet guncotton; its neutralising effect on any acid liberated during the storage of guncotton outweighs its slight saponifying action.

Silberrad and Farmer (Chem. Soc. Trans. 1906, 1759) have examined the hydrolysis of guncotton in alkaline solution. They find the reaction complicated by the reduction of some of the nitrate to nitrite, and the degradation of the cellulose to hydroxy- acids, &c.

Guncotton is reconverted into cotton by the action on it of alcoholic potassium sulphydrate. This reaction, due to Hadow, was found by Abel (*l.c.*) to give 53·6 p.c. to 55·4 p.c. cotton; trinitrocellulose should give 54·54 p.c. cotton. This reaction is of great importance, as it shows that guncotton (like nitroglycerin) is a nitric ester, yielding on reduction the hydroxylic body from which it was formed, and not an amino derivative. It can therefore be represented as:

$$C_6H_7O_2(ONO_2)_3.$$

Air-dried (air under ordinary conditions) guncotton retains between 1·5 and 2 p.c. of moisture. In this condition, on application of flame, a cylinder of compressed guncotton burns in the open air very rapidly with a long and fierce flame without smoke; the flame being coloured yellow by the sodium salts. The rate of combustion of the guncotton varies with its condition; thus, guncotton plait in the form of a flat tube burns very much more quickly than guncotton yarn. When dry and heated to about 100°, guncotton burns with almost explosive violence. The guncotton, as it leaves the hydraulic press, contains about 15 to 17 p.c. water, and is then not combustible; when held in a flame, it only smoulders as it partially dries.

Briskly heated in small quantity in the form of loosely twisted yarn, guncotton was found to explode at 150° (Abel). The exact ignition point varies with the physical condition of the guncotton and the method of determination.

Guncotton can be exploded by percussion; but when struck by an iron hammer on an iron

anvil, the portions directly struck by the hammer detonate, but the rest of the guncotton remains unexploded. Wooden boxes containing dry compressed guncotton, both closely and loosely packed, have been repeatedly fired at from rifles, the result being that the contents of the box were generally inflamed, but never exploded; while similar packages containing dynamite or other nitroglycerin preparations were always violently exploded by being fired at (Abel, Trans. Roy. Soc. 1874, 359–362). The use of moist guncotton has rendered any danger from shock still more remote.

Properly stabilised guncotton is a safe and permanent explosive when stored under normal conditions, especially when wet: many samples, well over 30 years old, have shown practically no signs of deterioration. Wet guncotton stored in air-tight vessels, especially wooden ones, is liable to the formation of fungoid and mould growths on its surface. The guncotton is frequently dipped in a weak alkaline solution of phenol to prevent these growths.

Under certain conditions, as when stored in contact with organic substances at rather elevated temperatures, guncotton may be decomposed by denitrifying bacteria, with the production of ammonia, nitrogen, and carbonic acid.

Products and heat of combustion. Guncotton does not contain sufficient oxygen for complete combustion into CO_2, H_2O, and N; the equation

$$2C_6H_7O_2(NO_3)_3+9O=12CO_2+7H_2O+6N$$

shows that cellulose trinitrate requires 24·3 p.c. more oxygen for complete combustion. Carbonic oxide and hydrogen are, therefore, naturally to be expected in quantity in the gases of combustion.

In the flaming combustion of guncotton, when the gases were allowed to escape freely at nearly atmospheric pressure, Sarrau and Vieille found a large quantity of nitric oxide, NO, in the gases; about one-fourth of the volume of the dry gases.

When the guncotton is inflamed in a closed vessel, in which the gases of combustion cause a moderate pressure, no oxide of nitrogen is formed. Von Karolyi exploded guncotton, in quantities of 10 grams, in small cast-iron cylinders of such strength as just to yield to the pressure of the gases produced by the combustion. These cylinders containing the guncotton were made air-tight, provided with the means of inflaming the guncotton by an electrically heated platinum wire, and enclosed in a spherical shell of about 5 litres capacity, which was exhausted before the explosion, and in which the permanent explosion gases of the guncotton produced an excess of pressure of about half an atmosphere, which enabled portions of the gases to be removed, by means of a stopcock, for analysis. Von Karolyi found the permanent gases to consist of CO_2 28·5, CO 39·8, CH_4 9·9, H 4·4, N 17·4 volumes per 100 (Pogg. Ann. April, 1863). Abel repeated Von Karolyi's experiments, and found acetylene always present in considerable quantity in the gases; an analysis of the permanent gases obtained from 10 grams of guncotton in two different experiments is given:—

Experiment 1: CO_2 19·69, CO 39·87, C_2H_2 7·85, CH_4 3·45, H 15·82, N 13·32 vols. per 100.

Experiment 2: CO_2 18·97, CO 41·80, C_2H_2 6·36, CH_4 3·87, H 17·02, N 11·98 vols. per 100.

Sarrau and Vieille (Compt. rend. 90, 1058) have ascertained the volume (at 0° and 760 mm.) and the composition of the permanent gases produced by the explosion of guncotton in a closed vessel, and find that both vary with the density of the charge $\left(\frac{\text{volume of guncotton}}{\text{capacity of vessel}}\right)$, *i.e.* with the pressure ensuing on the explosion. The following are some of the results obtained:—

	Density of charge	Volume of gases (at 0° and 760 mm.) given by 1 gram guncotton
(1)	0·01	658·5 cc.
(2)	0·023	670·8 „
(3)	0·2	682·4 „
(4)	0·3	—

Composition of the gases per 100 *volumes.*

	(1)	(2)	(3)	(4)
CO_2	21·7	24·6	27·7	30·6
CO	49·3	43·3	37·6	34·8
H	12·7	16·2	18·4	17·4
N	16·3	15·9	15·7	15·6
CH_4	none	trace	0·6	1·6

With these higher pressures, equivalent to higher temperatures, the composition of the gases is simpler; they contain neither acetylene nor oxide of nitrogen, and with increase of pressure there is increase of CO_2 and H and decrease of CO; oxidation of CO by H_2O evidently occurring, and the composition of the gases being the result of a balance between the oxidising action of H_2O on CO, and of the reducing action of H on CO_2.

Sarrau and Vieille, using Berthelot's formula for guncotton, equate its decomposition by explosion thus: $C_{24}H_{29}(NO_2)_{11}O_{20}$:

(*a*) When density of charge is 0·023:

$$=15CO+9CO_2+11H+9H_2O+11N;$$

(*b*) When density of charge is 0·3:

$$=13CO+11CO_2+15H+7H_2O+11N;$$

the reaction with high density of charge (which would be the condition in actual use) tends to approach the result:

(*c*) $12CO+12CO_2+17H+6H_2O+11N.$

The agreement of the equations with the results of analysis is, however, only moderately approximate.

For equation (*a*) the calculated quantity of heat evolved for constant pressure (for constant volume, the quantities of heat are about $\frac{1}{10}$ higher), and the volume of the gases reduced to 0° and 760 mm. (per 1 kilogram of dry and ash-free guncotton), are as follows, compared with Sarrau and Vieille's experimental values:—

	Quantity heat Calories calculated	found	Volume gas Litres calculated	found
Water, liquid	1076	1071	684	687·5[1]
Water, gaseous	997·7	—	859	—
For equation (*c*):				
Water, liquid	1074	—	743	—
Water, gaseous	1022	—	859	—

Guncotton, therefore, on explosion, gives (for equal weights) more gas and a greater quantity of heat than gunpowder or mining powder, more

[1] 671 litres from guncotton containing 2·4 p.c. ash.

gas but a smaller quantity of heat than nitroglycerin.

The heat evolved by the complete combustion of guncotton in oxygen gas, and under constant pressure, was found by Sarrau and Vieille to be per 1 kilogram of guncotton 2302 kgm.-degrees when the water formed was liquid, 2177 when gaseous.

Noble (Lecture to Inst. Civil Engin. April 3, 1884) obtained more permanent gases from detonated pellet guncotton than did Sarrau and Vieille with low densities of charge. Thus he states that 1 kilogram of guncotton (containing 2·36 p.c. moisture and 0·36 p.c. ash) produces, at 0° and 760 mm. pressure, about 730 litres of permanent gases (water, liquid); or, per 1 kilogram of dry and ash-free guncotton, about 750 litres of permanent gases. The gases were produced in the steel explosion vessel under very high pressure. The volume of gases agrees fairly well with that calculated for Sarrau and Vieille's equation (*c*) for high density of charge.

Noble states that the *temperature* of explosion of guncotton is at least double that of gunpowder; the latter temperature he estimates for ordinary English gunpowder at about 2200°.

The composition of the gases produced by the detonation of dry and of moist guncotton is given on p. 451.

Detonation.—Nobel, in 1864, had discovered that nitroglycerin could be *detonated* by means of mercury fulminate; and in 1868, Abel found that air-dry compressed guncotton (like nitroglycerin) could be *detonated* by the explosion in close contact with it of 5 grains (0·32 gram) of mercury fulminate, contained in a thin metal case (Trans. Roy. Soc. 1869, 159, 498). He subsequently (*ibid.* 1874, 337–395) found that by increasing the strength of the envelope, viz. by making the case for the fulminate of stout sheet iron, and inserting it in a closely fitting hole in the guncotton, the latter could be detonated with certainty with only 2 grains (0·13 gram) of the fulminate. In practice, however, much larger quantities of fulminate are used, in order to have a good initial detonation, and to provide for the possibility of the detonator tube fitting too easily into the hole in the guncotton.

The explosion of the guncotton thus caused by that of the fulminate has been called *detonation* on account of the loud sound by which it is followed; it differs from the flaming combustion of guncotton by the immensely greater speed at which chemical action (oxidation of one part of the compound, the C and H, by another part, the NO_3) progresses in the guncotton, and by the consequent powerful mechanical effects produced by the gases formed. Abel found the velocity of detonation of air-dry compressed guncotton to be about 18,000 feet per second; consequently, the large volumes of heated gases produced at this great rate work destructively on nearer objects, and give rise to a condensed wave in the air, propagated with great velocity. Moreover, the air offers resistance to the motion of the gases produced at so great a rate, consequently the gases exert pressure on the guncotton and on the ground or other support on which it rests, producing powerful reaction effects.

For the detonation of unconfined guncotton by mercury fulminate, it is essential that the former shall be in a condition to offer resistance to the shock of the fulminate, so that the energy of the shock shall heat the guncotton, not disperse it. Compressed guncotton meets this requirement, while in the form of wool or loose yarn it is scattered or inflamed, but not detonated.

Threlfall (Phil. Mag. 1886, 172) thus gives Berthelot's views on the theory of detonation: 'The kinetic energy of the shock of the explosion (by the detonator) is transformed into heat at the point (of the explosive) struck; the temperature of this point is thus raised to the temperature of explosion, a new shock is produced which raises the temperature of the neighbouring portions to the same degree; they then explode, and the action is thus propagated with an ever-increasing velocity.' The 'ever-increasing velocity' must refer to the commencing stage of the detonation, as Abel's measurements of the rate of detonation of guncotton and dynamite do not bear it out.

The detonation of guncotton is transmissible across an intervening air space which varies with the weight of the charge; thus the detonation of a ½ lb. cylinder of compressed guncotton, 3 inches in diameter, will cause the detonation of another similar cylinder placed on the ground at a distance of 1 inch, but not at a distance of 2 inches.

Silver fulminate is in no way superior to mercury fulminate in causing the detonation of guncotton. Nitroglycerin, nitrogen chloride and iodide show a remarkable want of reciprocity in their behaviour to guncotton as regards detonation. Thus, while the detonation of ½ oz. of guncotton caused the simultaneous detonation of a charge of nitroglycerin in a tin-plate vessel at the distance of 1 inch, and ½ oz. produced the same result across an air space of 3 inches, 1 oz. of nitroglycerin detonated in close contact with a disc of compressed guncotton did not detonate it, but only dispersed it. 100 grains of dry nitrogen iodide was unable to cause the detonation of a pellet of dry compressed guncotton on which it rested; and 50 grains of nitrogen chloride (covered with a film of water and contained in a thin watch-glass resting on the guncotton) was about the minimum quantity required to effect the detonation of the latter (Abel, Trans. Roy. Soc. 1869, 489).

With increase in the amount of water in the compressed guncotton, more mercury fulminate is needed to effect detonation; the fulminate as usual being contained in a tin-plate tube and fitting closely in a central hole in the guncotton. With a total of 5 p.c. of water (*i.e.* 3 p.c. above the 2 p.c. of normal air-dry guncotton), detonation by 15 grains of mercury fulminate is doubtful. Moist guncotton containing 12 p.c. water was detonated only once in seven experiments by a detonator containing 100 grains of fulminate; when the guncotton contained 17 p.c. water, it required 200 grains of fulminate to detonate it with certainty.

Guncotton as it leaves the press, containing about 15 p.c. water, although quite uninflammable, can be readily exploded by the detonation in contact with it of about half an

ounce of air-dry compressed guncotton. For the certain detonation of guncotton containing 20 p.c. water, a primer of about 1 ounce of dry guncotton is required; and when the guncotton has absorbed the maximum amount of water it is capable of doing (30–35 p.c.), for its certain detonation 4 ounces air-dry guncotton applied in close contact are necessary (Abel, Trans. Roy. Soc. 1874, 337). This discovery (which was due to Brown, of Woolwich Arsenal) has been of the greatest practical importance, as it has rendered the use of guncotton for military purposes very safe; permitting the great bulk of the guncotton to be kept in a moist and uninflammable state, while a relatively small quantity only of dry guncotton is needed for 'primers,' the dry primers being detonated by a suitable mercury fulminate detonator.

The velocity of detonation of moist guncotton is greater than that of the dry, and the work done by the same weight of guncotton appears to be equal, whether it be employed in the dry or moist state.

As in the case of dry guncotton, detonation is propagated in masses of moist compressed guncotton in contact, provided the piece first detonated does not contain less water than the others; but for transmission of detonation in the open air through any considerable number of cylinders or slabs of moist guncotton, it is essential that they should be in contact, much shorter air spaces than in the case of dry guncotton stopping the detonation.

The rate of detonation of moist guncotton is a little quicker than that of dry guncotton; and that of guncotton saturated with water (containing about 30 p.c. of it) is considerably quicker than that of the dry. Abel (Roy. Soc. 1874) measured (by means of Noble's chronoscope) the rate of detonation of guncotton under different conditions, of dynamite, and of nitroglycerin.

Cylinders of compressed guncotton 3 inches in diameter were employed; they were placed on their bases, and, when in a continuous train, with their circumferences touching, and the measurements of velocity of detonation were made at intervals of 6 feet, or sometimes of 4 feet, in the train of guncotton. The following are some of the results obtained:—

—	Rate of progression of the detonation: feet per second		
	First 6 feet.	Last 6 feet	Mean (of all the measurements)
Dry guncotton, 170 cylinders, touching	17,466 4 feet	17,738 4 feet	17,122
„ „ ½-inch air spaces, 28 feet	15,676 4 feet	16,218 4 feet	16,776
Moist guncotton (15 p.c. water), 28 feet, touching	18,416	18,040	18,375
Wet guncotton (30 p.c. water), 36 feet, touching	22,574	19,240	19,948
Dry guncotton, containing 38 p.c. KNO_3, touching	—	—	15,981

The above results show that there is a decided increase in the rate of detonation of guncotton, when the air in the latter is replaced by the very slightly compressible water—a behaviour recalling the greater velocity of propagation of sound in water than in air.

The velocity of propagation of sound, too, comes nearest to the detonation-velocities just given; thus the experimental values for sound (of low intensity) in water at 8° is 4708 feet per second, and in ice is 9512 feet.

Wet guncotton, when frozen, is detonated with certainty by the fulminate detonators ordinarily used for dry guncotton (Abel, *v. supra*).

The gases resulting from the detonation of dry and of wet compressed guncotton were examined by Noble and Abel, and from their results the two following analyses are taken. The detonation was effected in a very strong steel explosion vessel, in which the gases were formed under very great pressure. A correction should be made in the dry guncotton gases for the permanent gases ($2CO+2N$) of the mercury fulminate detonator, and for the same and those from the small quantity of dry guncotton priming in the case of the wet guncotton gases; but as the CO would be oxidised by the gaseous water to an unknown extent, the direct results are given.

Composition of the permanent gases, vols. per 100.

	Dry guncotton, 1620 grains pellet, 130 grains mercury fulminate detonator	Wet guncotton
CO_2	24·24	32·14
CO	40·50	27·12
H	20·20	26·74
N	14·86	14·00
CH_4	0·20	none
	100·00	100·00

It is noticeable that Sarrau and Vieille's results for the composition of the gases of explosion of guncotton for the lower density of charge (*v. supra*) approach the composition of these detonation gases of dry guncotton. The influence of the additional water on the gases of detonated wet guncotton, in oxidising CO to CO_2 with formation of H, is very marked.

For the condition of gaseous water, a greater quantity of heat will be evolved by the detonation of dry guncotton than by that of moist guncotton containing the same weight of the dry material; the volume of the gases will, however, be greater from the moist than from the dry guncotton. The volume of the permanent gases also will be greater with moist guncotton, owing to the H formed from the water.

Von Forster, in Germany, for special military use, coats pieces of moist compressed guncotton with a skin of dry guncotton by immersing them for about a quarter of a minute in ethyl acetate.

It has also been proposed to use paraffined guncotton instead of moist guncotton, prepared by immersing dry compressed guncotton in melted paraffin. The paraffin has the advantage over water that it does not evaporate; it is said to make dry guncotton less sensitive to shock, but it lowers the percentage of oxygen, and is stated to be inflammable.

Intensity of action.—Abbot, in his Report, gives the intensity of action of compressed guncotton, detonated under water, as 87, kieselguhr dynamite No. 1 being 100. In comparative experiments made in this country, under different conditions to Abbot's, guncotton has shown a slightly greater intensity than dynamite; as, for instance, in the displacement of earth by the detonation of buried charges, and in the work of excavation done by their detonation in the borehole of lead cylinders. Abel's experiments, by the latter method, give the intensity of action of guncotton as 101, the dynamite being 100; experiments in which the same weight of fulminate was used being compared.

Uses.—Guncotton is almost exclusively employed for military purposes, for use in offensive torpedoes and in submarine mines, and for demolitions on land. It is also used in the manufacture of smokeless powders, both military and sporting, and in certain fuses and fuse compositions.

Guncotton mixtures. It has already been mentioned that 100 lbs. $C_6H_7O_2(NO_3)_3$ require 24·3 lbs. additional oxygen for complete combustion into CO_2 and H_2O; and guncotton, on account of the lower nitrates present, would require more oxygen. At an early period in the history of guncotton, this oxygen was supplied in the form of potassium or other nitrate. Potassium chlorate was also suggested but abandoned, owing to the lack of stability of the mixture, although the explosive effect of the guncotton was largely increased.

Potentite is a mixture of guncotton and potassium nitrate.

Tonite, invented by Trench, is manufactured by the Cotton Powder Co. at Faversham, and also at San Francisco. It was originally intended to be used as a propellant, but is now only used as a disruptive explosive. *No.* 1 is an intimate mixture of about equal weights of wet guncotton pulp and barium nitrate, the paste being compressed into cartridges with the usual recess for the detonator, and wrapped in paraffined paper. *No.* 2 is a mixture of guncotton, potassium and sodium nitrates, charcoal, and sulphur; and *No.* 3, a mixture of 18–20 p.c. guncotton, 11–13 p.c. dinitrobenzene, and 67–70 p.c. barium nitrate, and 0·5–1 p.c. moisture. Tonite was used in the construction of the Manchester Ship Canal. *No.* 1 is used for blasting hard rock. *No.* 3 is slower in its action, and is used for soft rocks. It is also used for military purposes.

Tonite burns slowly and without tendency to explosion on ignition. It detonates readily and completely, and there is practically no carbonic oxide in the products of detonation.

Abel found its intensity of action, by the lead cylinder method, to be 84, kieselguhr dynamite No. 1 being 100.

Abbot (Addendum I. to his Report) examined tonite of San Francisco make, consisting of 52·5 p.c. guncotton and 47·5 p.c. barium nitrate. Detonated under water, it gave intensity 81, dynamite being 100.

Whilst the intensity is lower than that of guncotton, these values show that the guncotton is remarkably economised in tonite. To render tonite safe for use in fiery mines, the cartridges are surrounded by a layer of 'Trench's Fire-extinguishing Compound.' This is sawdust impregnated with a mixture of alum, ammonium chloride and sodium chloride, and extinguishes all flame from the tonite on detonation of the latter.

Other guncotton mixtures are included under 'Smokeless Powders.'

Collodion cotton. By collodion cotton, for the purposes of explosives, is meant soluble nitrocotton. It is less highly nitrated than guncotton, and at the present time is looked upon as a mixture, in varying proportions, of the di-, tri-, tetra-, and penta-nitrocelluloses of Eder's classification.

It is possible to prepare soluble nitrocotton of a definite nitrogen content, by working under definite conditions as to composition of acid mixture, and temperature, and time of nitration. For smokeless powders and the gelatin dynamites, a nitrocellulose soluble in nitroglycerin or other solvents, containing as high a percentage of nitrogen as possible, 12·5 to 12·7 p.c., is desirable, and also one capable of holding the nitroglycerin bound, so that it does not exude under varying climatic conditions.

Manufacture.—In the manufacture of collodion cotton, the finer qualities of white cotton waste are used. The mixed acids are much weaker than in the manufacture of guncotton, and the temperature of nitration is higher. Lunge, however (*l.c.*), found that the quality of the cotton had little or no effect on the quality of the collodion cotton obtained. He also concludes that 40° is the most suitable temperature for obtaining a maximum yield of maximum degree of nitration and solubility, and that the maximum content of nitrogen in the product is obtained when the ratio of sulphuric acid to nitric acid is not less than 0·25 : 1, and not more than 3 : 1.

The acid mixture usually used contains about 66 p.c. H_2SO_4, 23 p.c. HNO_3, and 11 p.c. H_2O; and the nitration is usually carried on for between 1 and 1½ hours at a temperature of about 40°. However, the exact acid mixture and temperature and time of nitration vary considerably in different factories, and sometimes collodion cotton is made in the cold by using an appropriate nitrating mixture.

The nitration is performed in either lead or iron nitrating pots or tanks, or in centrifugals, and the extraction of acid, washing, pulping, and other processes are carried out in the same way as with guncotton.

Properties.—Collodion cotton should be completely soluble in ether-alcohol and in nitroglycerin. It is also soluble in the solvents of guncotton. Bernadou states that when collodion cotton is immersed in ether and kept at a

temperature below 0°, it passes into solution or forms a colloidal jelly. Its exploding temperature is higher than that of guncotton, and its explosive effect much less.

Smokeless Powders.

History.—Attempts were made by the inventors and early workers in guncotton, notably in Austria, to adopt it as a propellant. Schönbein and Otto, in 1846, attempted to use guncotton in rifles, and von Lenk, in 1862, prepared cartridges of spun and woven guncotton for use in cannons. The guncotton was much too rapid and violent in its action, even when woven or compressed, and none of these early experiments was successful.

Abel, in 1865 (Eng. Pat. 1102, 1865), patented a process for granulating guncotton with a solution of gum, and also proposed to use a mixture of guncotton and collodion cotton treated with a solvent; and Kellner, of Woolwich Arsenal, at about the same time, made a granular smokeless powder from guncotton; but these powders did not get beyond the experimental stage.

A semi-smokeless powder was invented by Schultze, in 1865, who used nitrated wood granulated with a saturated solution of barium and potassium nitrates; and Volkmann, who worked Schultze's patent near Vienna, treated the grains with a mixture of ether and alcohol, and practically made a modern gelatinised smokeless powder. The manufacture of this powder, however, was prohibited, as it infringed the gunpowder monopoly of the Austrian Government. Schultze's powder is still in use for sporting purposes.

The difficulty in adopting guncotton as a propellant was its porosity, for when the powder was ignited, the flame was forced into the interior of the grains, and caused the whole charge to explode, instead of burning progressively. Many attempts were made to reduce the rate of combustion by compression, and by mixing the guncotton with inert ingredients, such as unnitrated cotton, or coating the grains with paraffin, stearin, or indiarubber, and more or less successful sporting powders were produced in this way. Prentice, in 1866 (Eng. Pat. 953) suggested a sporting powder made of pyropaper, containing 15 parts of unnitrated cellulose; and Punchon proposed to regulate the speed of combustion of guncotton by soaking in a solution of sugar, and added nitrates to increase the explosive force (Eng. Pat. 2867, 1870).

In 1882 Reid (Eng. Pat. 619, 1882) patented a process for the granulation of a mixture of soluble and insoluble nitrocellulose, and hardening the grains with ether-alcohol; the product, known as 'E. C. Powder,' is too violent in its action for military purposes, but is still largely used as a sporting powder. 'J. B. Sporting Powder,' afterwards introduced by Johnson and Borland (Eng. Pat. 8951, 1885), was a mixture of collodion cotton with potassium and barium nitrates, hardened by a solvent of the nitrocellulose and subsequent drying.

Some form of military smokeless powder became essential on the introduction of small-bore magazine rifles, and efforts were again made in 1885 to retard and regulate the combustion of nitrocellulose by converting it into a product absolutely devoid of all porosity. The sporting powders in use at the time were only superficially hardened, and contained fibrous nitrocellulose, but eventually Vieille, in 1886, introduced 'Poudre B,' named after General Boulanger, a completely gelatinised, dense, horny, and non-porous explosive, made by treating a mixture of guncotton and collodion cotton with ether-alcohol, and this was adopted by France as a propellant for the Lebel rifle.

Other countries at once began to work on similar lines, and Germany adopted a similar powder. But Nobel, after the invention of blasting gelatine, tried to utilise nitroglycerin as an ingredient for a smokeless propellant, and eventually patented 'Ballistite' in 1888 (Eng. Pat. 1471, 1888), a colloid mixture of collodion cotton and nitroglycerin, which at first also contained camphor. This powder was adopted by the Italian Government. About the same time, an English Explosives Committee was working on the same subject at Woolwich, and gradually evolved a nitroglycerin smokeless propellant, which was adopted by the British Government under the name of 'Cordite' (Eng. Pat. 11664, 1890). Cordite is a mixture of guncotton and nitroglycerin, with a small proportion of mineral jelly.

Some form of smokeless powder was rapidly adopted by all civilised countries for small-arm purposes, and since that time the manufacture, composition, and form of the explosives have been gradually modified and so perfected that, at the present time, accurate and reliable smokeless powders are available and solely used as propellants even for the heaviest ordnance.

The general principle in the manufacture of all these smokeless powders is to thoroughly gelatinise the nitrocellulose by means of some solvent, so that its fibrous character is destroyed.

The powders are more or less hard, homogeneous colloids, which only burn progressively from the surface, so that their combustion is completely under control.

Composition.—Smokeless and semi-smokeless powders can be roughly divided into the following classes, according to their composition: (1) Nitrocellulose powders, which may be composed of collodion cotton or guncotton or a mixture of the two. (2) Nitrocellulose powders with oxidising salts, in which one of the divisions of class (1) is mixed with a metallic nitrate, and perhaps other ingredients. (3) Nitrocellulose-nitroglycerin powders, where one of the divisions of class (1) is combined with nitroglycerin. (4) Nitrocellulose powders combined with another nitro derivative, with or without nitroglycerin and metallic nitrates.

Military smokeless powders. Although powders belonging to all these classes have been tried for sporting purposes, and many of them also for military purposes, so far as the latter are concerned, there are to-day only two varieties of smokeless powders, nitrocellulose powders and nitrocellulose-nitroglycerin powders.

The smokeless powders of the latter class are more powerful than the pure nitrocellulose powders, for the nitroglycerin supplies the oxygen, that is deficient in guncotton, for complete combustion. A smaller charge and

consequently a smaller gun chamber are necessary with the nitroglycerin powders for equal ballistic results. The solvent is more readily eliminated when the powder contains nitroglycerin, and the powders are cheaper; but the temperature of combustion is higher, and, with a large proportion of nitroglycerin, the consequent erosion of the gun is serious. Nitrocellulose powders tend to give irregular ballistics, owing to their sometimes more porous nature and frequent physical instability on storage, and sometimes quite a small proportion of nitroglycerin is added to remedy this defect.

Secondary ingredients.—Besides the main ingredients, nitrocellulose and nitroglycerin, military smokeless powders usually contain small quantities of other substances added for attaining some special purpose. These secondary ingredients may be added as moderants or deadeners, stabilisers, or cooling agents.

Moderants or deadeners are added to reduce or control the rate of combustion of the explosive. Amongst these substances may be mentioned camphor, vegetable oils, such as castor oil; and mineral hydrocarbons, such as paraffin and vaseline.

Stabilisers.—The addition of a small quantity of alkali was frequently made in the early days of smokeless powders to combine with any acid developed in them on storage. This addition of alkaline neutralising agents was, however, soon shown to be harmful, because they are liable, under certain conditions, to hydrolyse the nitrocompounds.

This is true even of so mild an alkali as calcium carbonate. Alkaline neutralisers yield nitrites, which decompose again at elevated temperatures, and so act catalytically in decomposing the nitrocellulose.

Residual solvent was found to stabilise the powders to a considerable extent by absorbing the products of decomposition; and to prevent rapid loss by evaporation, solvents of high boiling-point were used, for instance, a little amyl alcohol was added to an ether-alcohol solvent. The elimination of the solvent leaves the powder porous and so accelerates the rate of decomposition.

The more usual method of stabilising is to add a small quantity of some substance that will form a stable compound by chemically combining with any liberated peroxide of nitrogen, and so act so long as any of the free substance is left. Aniline, diphenylamine, aminoazobenzene, nitroguanidine, and similar compounds are added for this purpose. The vaseline in cordite, although originally added for another purpose, has been proved to have a marked stabilising influence. Soaps, resins, and oils have also been suggested as stabilisers.

The French Commission, on the explosion of smokeless powder on the 'Jena' in 1907, drew attention to the fact that substances like diphenylamine and aniline not only act as stabilisers, but also as *indicators* of decomposition, owing to the formation of local spots or patches of peculiar colours, and such substances have been increasingly used for this purpose since that time.

Cooling agents.—Most smokeless powders have a high temperature of explosion, which not only causes erosion of the bore of the gun, but also gives a strong and readily visible flame. The more complete the combustion, the higher the temperature of explosion, and simple alteration of proportions of the ingredients of a nitroglycerin and nitrocellulose explosive, so as to render the combustion less complete, will give a lower temperature and less flame, as is instanced by "modified cordite." The substances added as moderants (oils, fatty and mineral, wax, resin, camphor, &c.) tend in the same direction, and the addition of charcoal has also been proposed. With these additions, the products of combustion contain more carbonic oxide and hydrogen, and the actual temperature of explosion is less. The addition of a sufficient quantity of these substances to adequately reduce the temperature of explosion causes a serious reduction of the explosive power. The use, in comparatively large quantity, of substances like guanidine nitrate, nitroguanidine, and substituted ureas, has been claimed to reduce the temperature of explosion without reducing the ballistics of the powder.

With incomplete combustion, however, the carbon monoxide and hydrogen inflame on coming in contact with the air, and, burning together with any unburnt charge, produces a very decided flame. To produce a *flameless explosive*, substances are added so as to mix the products of explosion with a sufficient proportion of non-inflammable gas to protect the inflammable gases from the atmosphere until their temperature has fallen below their ignition-point. The problem is similar to the production of a safety detonating explosive for use in fiery coal-mines, and similar remedies have been proposed.

Duttenhofer (Eng. Pat. 24782, 1904) proposed the addition of an alkaline bicarbonate, claiming that it had no detrimental effect on the stability of the explosive, as is the case with the normal carbonate. It cools the flame by the liberation of its water of crystallisation and carbon dioxide. In a later patent, Luciani (Fr. Pat. 380963, 1906) proposes a mixture of carnauba wax, bees-wax, and sodium bicarbonate. Edwards (Eng. Pat. 24025, 1907, and 12188, 1908) proposes a similar mixture, in which the sodium bicarbonate may be replaced by the ammonium or magnesium compounds; and Vender (Fr. Pat. 405822, 1909) claims for hydrated magnesium carbonate or manganese peroxide. Oxalic acid and its salts have also been tried, but a really suitable ingredient for decreasing the flame of smokeless powders in guns of large calibre has however not yet been found.

Solvents.—The solvents used in the gelatinisation of smokeless powders are usually acetone, ethyl acetate or amyl acetate for guncotton powders, and a mixture of ether and alcohol for the collodion cotton powders.

Powders gelatinised with ether-alcohol are very liable to blister, curl up, and become distorted during drying, owing to the rapid evaporation of the ether, and there is difficulty in driving off the amyl acetate owing to its high boiling-point. The correct proportion of solvent has to be carefully worked out for individual powders. Too much solvent increases the difficulty of drying, and increases the liability to distortion and cracking, whilst too little delays the mixing and renders it imperfect.

The secondary ingredients are usually dissolved in the solvent before it is added to the main ingredients.

Heating with camphor under pressure, instead of treatment with solvents, gelatinises and hardens soluble nitrocellulose powders, but this substance, as it remains as a constituent, causes physical instability owing to its volatility, and its use has been abandoned. The solvents used in the gelatinisation do not, as a rule, remain in the finished powders except in very small quantity.

Manufacture.—Only a general outline of the manufacturing processes is given here: the details vary, and some are given under individual powders.

The drying of the nitrocotton.—This is one of the most dangerous operations in the manufacture of smokeless powder, especially when the last portions of the moisture are being driven off. Any dry dust is very susceptible to ignition by friction or shock, and the dry nitrocotton is readily electrified even by a current of dry air, and special precautions have to be taken to connect the drying trays to earth, the necessity for which was first pointed out by Reid. The nitrocellulose is sometimes dried by removing part or the whole of the water by treating it with alcohol. This process was used in 1891 in Austria, and was patented in England by Durnford in 1892. To render the nitrocellulose anhydrous, it is first soaked in alcohol that has been previously used, squeezed and pressed, and then treated similarly with fresh alcohol. A further advantage of this process is that some unstable impurities may be eliminated by this washing with alcohol.

Mixing and incorporating.—The nitrocellulose should be in as fine a condition as possible. The first wetting with the solvent is a difficult matter, and is sometimes effected *in vacuó*. The absence of all dust, when once the solvent is added, makes the manufacture of smokeless powders much safer than that of gunpowder. Even if ignition occurs, the combustion, though fierce, never leads to explosion, and is usually very local in its effects.

The incorporation is usually carried out in kneading machines, but sometimes by rolling. The kneading machine almost exclusively used is that of Werner, Pfleiderer, and Perkins. It consists of an iron trough, the upper part of which is rectangular. The bottom is in the form of two parallel half-cylinders, in which two heavy screw-shaped paddle-blades revolve in opposite directions, one at about twice the rate of the other. The allowance between the blades and bottom is small and the mixture is thoroughly kneaded and mixed between them and the trough. The mass becomes considerably heated during the kneading, and to prevent loss of solvent, the machine is covered and the bottom is surrounded by a cold-water jacket. It is necessary to connect the mixing machines to earth, as in the case of the drying trays.

When the material is to be worked into sheets, the rolling is effected in two operations, the first to effect incorporation of the materials, and then between closer set rollers to reduce the sheets to the requisite thickness. For powders of the ballistite type, the rollers are hollow and steam heated. The sheets are then dried to drive off greater part of the solvent, and again rolled to eliminate any blisters formed during the drying. Thick sheets are produced by folding the thin sheets over and over and passing them backwards and forwards between the rolls, by which means a homogeneous thick sheet is obtained.

Cutting and pressing.—The partially dried sheets are usually cut into small square plates. The machines generally used are similar to those in use at the German Government factory at Spandau, in which two sets of revolving circular cutting knives, slightly overlapping, cut the sheet into strips, which are then fed over a fixed cutting edge, and chopped into plates or cubes by a set of rotating knives. Round flakes and discs are cut from cords. After cutting, the grains are further dried.

Cord and tube powder is usually pressed through dies, as in the manufacture of cordite, the material being sometimes subjected to a preliminary rolling to exclude air bubbles, but the Austrian rifle powder is stated to be drawn and not pressed. For producing the tubular and multi-perforated powders, one or more pins are arranged so as to project into the holes of the dies.

Drying.—The powders are dried slowly in stoves, at a temperature of about 40°. The time of drying depends on the size and shape of the grains, but usually lasts several days. In modern factories, the drying stoves are air-tight, and the current of hot air is drawn, by means of fans, through special apparatus for recovering the solvent. In some cases, the solvent is largely eliminated by boiling the shaped powder in water.

One of the drawbacks of pure nitrocellulose powders is the difficulty of eliminating the solvent in a reasonable time, especially from the larger sizes, without causing the development of cracks on the surface of the grains. Sometimes a rather large proportion of solvent is left in the powder, but then on storage the solvent evaporates, and cracks may also form and so render it impossible to attain the constancy of ballistics necessary in a military powder. The solvent can be more easily removed from nitroglycerin powders, and the higher the percentage of nitroglycerin the more rapidly and more efficiently can the solvent be eliminated.

The flake small-arm powders are usually graphited, so that the grains may run freely through the cartridge-loading machines.

Blending.—To ensure uniformity of ballistics, the different batches of powder are thoroughly blended.

Sporting smokeless powders may be broadly divided into two classes—bulk powders and condensed powders.

The bulk powders have a low density, and are designed so that a charge may have the same bulk as black gunpowder to give the same velocity and pressure. They are used mainly in shot guns, and only to a limited extent in sporting rifles. The grains are loose and only surface hardened by means of a solvent. They are usually composed of soluble nitrocellulose, mixed with either potassium or barium nitrate, and are generally worked up in an incorporating mill. The mixture is usually granulated either by sprinkling with water and rotating in a drum

or by spreading out on a rapidly oscillating table, but sometimes the mixture is slightly compressed and afterwards broken up into grains. In all cases, the solvent is sprinkled over the powder after granulation.

The condensed powders have a high density, and the charge occupies only one-third to one-half that of a gunpowder charge. They are used only in specially designed modern weapons. These powders are completely gelatinised, and are made in a similar way to the military flake small-arm powders. The powder paste is rolled into thin sheets, which are cut up into small flakes, and the grains dried as usual.

Occasionally sporting powders are made by an intermediate process, the grains being thoroughly gelatinised. The powder, wet with solvent, is treated with steam, so that the solvent rapidly evaporates and leaves the grain in a bulky form, but the nitrocellulose is hardened throughout the mass, and waterproofed.

Properties.—Pure nitrocellulose powders are grey to yellow, and nitroglycerin powders yellow to brown in colour. They are sometimes coloured by the secondary ingredients, or dye substances may be added, and the grains, more especially those of smaller size, are frequently coated with graphite, giving them a grey to black colour. The surface is usually smooth, but sometimes matted. The powders usually have the consistency of horn, but those containing nitroglycerin are softer and more readily cut than the pure nitrocellulose powders. The specific gravity of the powders varies with their composition and mode of manufacture, but the gravimetric density of the small flakes or grains is usually between 0·25 and 0·40.

The shape of the grains varies considerably. Sporting powders are usually in grains or very thin flakes; military small-arm powders either in thin squares, rectangular plates or discs, or in small cubes, thin cords, or narrow ribbons. The powders for large guns may be in the form of ribbons, thick cords, round or square sectioned, large cubes, tubes, or cylinders, the size and shape of the grain being adapted to any particular-sized gun, so that the highest possible muzzle velocities may be obtained without excessive pressures. The larger the grain, the less the initial burning surface per unit weight, and the slower burning the charge. The thicker cords and cylinders are frequently perforated through their length by one or more fine holes. The length of the perforated cords must not be too great, or they break up into fragments under the pressure developed in a gun, and the excessive pressures developed may burst the gun. If very long, tubes will even burst when fired in the open. Sometimes long perforated cords have transverse cuts or perforations made in them at intervals to facilitate the escape of the gases and prevent the bursting.

Irregularity of ignition causes irregular burning and pressures. Flakes, strips, and sheets may ignite and burn irregularly, owing to the grains adhering together. To prevent this irregular ignition and burning, the flakes are frequently cupped, and the strips and sheets have grooves cut in them, or have ridges moulded on their surface.

To vary the rate of burning, the grains are sometimes coated with a non-explosive, such as a wax, or a semi-explosive, like dinitrotoluene, and grains built up of layers of different rates of burning, the inner being the more explosive, have been suggested.

Stability, physical and chemical, under all conditions of climate, storage, and use, is one of the most desirable qualities in a military explosive. Smokeless powders usually contain small quantities of moisture or residual solvent. This has a considerable influence on the shooting qualities of a powder, and has to be carefully regulated in quantity. The effect of excess of solvent, especially on the nitrocellulose powders, in causing physical instability has been already pointed out. Pure nitrocellulose or nitroglycerin-nitrocellulose powders are not affected by moisture, but all nitrocellulose powders are subject to slight deterioration on storage, the deterioration being a function of the temperature, increasing with rise of temperature. The chemical stability of military powders is tested on manufacture and at frequent intervals (*see Stability tests*). Nitroglycerin powders may exude nitroglycerin on cold storage, but it is usually re-absorbed at normal temperatures.

Smokeless powders require smaller charges and gun chambers to produce equal velocities with black gunpowder, and the pressures are more slowly developed and better sustained whilst the shot is in the bore of the gun. This gradual development of the pressure depends on their colloidal nature; the grains when ignited only burn in successive layers, even under the high pressures developed in a gun. An ideal propellant should have a low maximum pressure, slowly developed and maintained so long as the projectile is in the bore of the gun, and should be completely consumed at the moment the projectile leaves the bore.

The regularity of the shooting of smokeless powders, after regularity of ignition, depends on the purity of the materials and the perfection of the manufacture. All powders are carefully blended, and subjected to analysis and a test for pressures developed and velocities obtained before acceptance.

Smokeless powders are very insensitive to shock and percussion; they are not fired by the passage of a bullet through them. Even those powders with a high percentage of nitroglycerin cannot be detonated by means of a strong detonator, unless there is much unabsorbed nitroglycerin present. They are somewhat difficult to ignite, and sometimes ignite irregularly, owing to their horny nature and smooth surface. Small-arm powders require more powerful caps than black gunpowder, and the larger charges require priming with gunpowder or guncotton to make ignition certain. The ignition point of gelatinised nitrocellulose powders is about 175°–180°, and of nitroglycerin-nitrocellulose powders about 180°–185°, when the temperature is raised rather rapidly. The ignition point is lowered by heating up slowly, and even a trace of acid has a considerable effect in lowering the ignition-point.

The solid residue from smokeless powders and its effect on the formation of rust in small arms has been examined by van Pittius (Zeitsch. angew. Chem. 1906, 848). He found that a graphited pure nitrocellulose powder gave about 0·11 p.c. of a faintly alkaline residue. The matter

insoluble in water was 0·01 p.c., and contained graphite, oxides of copper and iron, and traces of antimony sulphide. The soluble residue, 0·1 p.c. on the powder, contained 17 p.c. potassium ferrocyanide, 17 p.c. ammonium carbonate, 13 p.c. ferric chloride, 31 p.c. potassium carbonate, 10 p.c. calcium chloride, 7 p.c. copper sulphate, and 5 p.c. potassium antimoniate. The residue contained no nitrates, nitrites, chlorates, cyanides, or sulphides. A graphited nitrocellulose-nitroglycerin powder, 40 : 60, gave about 2 p.c. of a faintly alkaline residue of which only about $\frac{1}{30}$th was insoluble in water, and contained graphite and oxides of iron and copper. The soluble residue contained 51 p.c. potassium carbonate, 38 p.c. potassium chloride, 11 p.c. potassium antimoniate, and traces of iron and sulphate. There were no nitrates, nitrites, chlorates, cyanides, ferrocyanides, sulphides, or ammonium salts present. In the residues, the antimony, potassium, sulphate, and chloride, actually come from the cap composition, the iron largely from the gun and the copper from the bullet.

After experimenting with various solutions, Pittius concludes that the residue from the powders are not in themselves rust producers, but become so after a time, as they are hygroscopic. Frequent washing out of the gun and subsequent oiling with a viscous lubricant will be sufficient to prevent rusting.

The erosion of the bore of the guns caused by smokeless powders is almost entirely conditioned by the temperature developed in their explosion, and not to any corrosive action of the products of combustion. It is greater with the powders containing nitroglycerin than with the pure nitrocellulose powders.

The gaseous products of combustion of smokeless powders are water vapour, carbonic acid gas, carbonic oxide, hydrogen, nitrogen, and a small quantity of marsh gas. Sometimes oxides of nitrogen are formed when the explosion is imperfect. They may be always produced at the moment of explosion and be subsequently reduced by the large volume of carbonic oxide and hydrogen at a high temperature.

The heat of explosion and products of combustion of several commercial varieties of smokeless powder have been determined by the ordinary calorimetric bomb method, by Macnab and Leighton, and the following table showing some of their results is taken from a paper read by them before the Society of Chemical Industry, in March, 1904 (J. Soc. Chem. Ind. 1904, 298):—

Powder	Calories per gram	Permanent gas per gram 0° and 760 mm.	Water vapour c.c. per gram	Total gas c.c. per gram 0° and 760 mm.	Percentage composition of permanent gas				
					CO_2	CO	CH_4	H	N
Imperial Schultze	742	763	152	915	8·9	52·7	1·0	27·0	10·4
Amberite . .	745	635	156	791	12·0	50·0	0·4	25·5	12·1
S.S. . . .	755	695	131	816	11·8	51·3	0·8	23·7	12·4
E.C. . . .	762	718	158	876	11·9	52·1	0·5	23·9	11·6
Schultze . .	786	576	160	736	15·5	46·7	0·8	23·0	14·0
Kynoch's smokeless	807	600	126	726	14·8	49·5	0·7	18·8	16·2
Cannonite . .	845	725	146	871	14·6	49·9	0·6	22·2	12·7
Shot-gun rifleite .	896	705	169	874	19·0	45·3	0·8	21·5	13·4
Walsrode . .	1014	669	206	875	21·3	48·2	0·4	10·1	14·8
Cordite M.D. .	1031	726	215	941	16·3	50·4	0·0	19·7	13·6
Cordite . .	1253	647	235	882	24·9	40·3	0·7	14·8	19·3
Sporting ballistite	1286	591	234	825	32·2	37·1	0·4	10·1	20·2

Under the conditions of the experiments no oxides of nitrogen were formed. The authors call attention to the fact that the quantity of heat developed in the nitrocellulose powders increases with the nitrocellulose content, and that a large increase takes place when nitroglycerin is present. Other conclusions are, that as the heat increases, the quantity of carbon dioxide increases, the carbon monoxide and hydrogen decrease, and a larger quantity of water vapour is formed.

The relative temperatures of explosion of these powders were determined by a thermo-electric pyrometer method described by Macnab and Ristori in 1900 (Proc. Roy. Soc. 66, 221). The order of the powders according to the temperature developed was, broadly speaking, the same as that given by the total heat of combustion.

The constants of explosion of several smokeless powders have been exhaustively examined by Noble, showing their relationship to the density of loading (*see* Proc. Roy. Soc. 1905, 381, 512 and 1906, 453). With the density of charge varying from 0·05 to 0·50, Noble found that, as a general rule, with increase of resulting temperature and pressure, there was at first a slight increase and then a steady decrease in the volume of the permanent gases, also a large increase in the volume of CO_2 and decrease in the volume of CO. The volume of H decreases with increasing pressure, while that of CH_4 rises rapidly. He also found that the amount of erosion depended almost entirely on the heat developed, and was independent of the pressure.

Only a few smokeless powders can be referred to in any detail. With many powders the details of composition and manufacture are desired to be kept secret; and of the details characteristic of any powder, only those are given which have been already published.

The military smokeless powders, especially,

are constantly undergoing modifications and improvements and frequently different compositions, nitrocellulose or nitrocellulose-nitroglycerin powders of different degrees of nitration and proportions, are in use at the same time by a country for military purposes, according to the calibre of the gun in which they are to be used, and according as the powder is required as a propellant or for blank ammunition.

As far as the military small-arm powders are concerned, England, Italy, and Norway generally use nitroglycerin powders, other countries nitrocellulose powders.

(1) *Nitrocellulose Powders.*

Poudre B., or Vieille powder, was the pioneer of military smokeless powders. As invented by Vieille, in 1886 (Mém. des Poudres et Salpêtres, 1908–9), it was a mixture of soluble and insoluble nitrocellulose, thoroughly gelatinised with a mixture of ether and alcohol, rolled into sheets and then cut into strips. It sometimes contained about 2 p.c. paraffin. It had a nitrogen content of about 12·7 p.c. Amyl alcohol was subsequently added in varying proportions up to 2 p.c. as a stabiliser in the powders AM_1 and AM_2. 1·5 p.c. of diphenylamine was also tried as a stabiliser, but a powder containing 8 p.c. of amyl alcohol has shown better keeping qualities than those containing diphenylamine.

E. C. powder, a bulk sporting powder, as originally invented by Reid, was a pure nitrocellulose powder, superficially gelatinised with ether-alcohol and coloured orange with aurine. The E. C. powders are now manufactured by the E. C. Powder Co. at Dartford, under the patents of Johnson and Borland, already mentioned, and contain a more highly nitrated cotton, with potassium and barium nitrates and sometimes camphor and wood meal.

Walsrode powder, one of the earliest granulated sporting powders, made by Wolff and Co. of Walsrode, is a pure nitrocellulose powder gelatinised with ethyl acetate. The grains were formed, and the solvent eliminated by adding water to the kneaded mass and introducing steam, and subsequent boiling in water; the grains were then centrifugated and dried. The granulation is now effected differently, but the essential treatment is the same. The finished powder contains about 1 p.c. of volatile matter and 98·5 p.c. of nitrocotton.

M. N., or Maxim-Nordenfelt, powder is an American guncotton powder gelatinised with ethyl acetate.

Normal powder manufactured by the Swedish Powder Co. of Landskrona, and adopted by the Swiss Government, is a gelatinised guncotton powder made in various forms. Ethyl acetate is the gelatinising solvent. The small-arm powder was at one time in the form of small, light-grey, graphited square tablets of about 1·25 mm. side, but now small cylinders, of about 1 mm. diameter and length are used. It contains about 1·5 p.c. of residual solvent, and about 95 p.c. guncotton.

Von Förster powder (Fr. Pat. 164792, 1884) and *Troisdorf powder* are gelatinised nitrocellulose flake powders, the former containing a little calcium carbonate.

Wetteren powder, made by Cooppal, and used as the Belgian Service powder, is a guncotton powder, containing a little calcium carbonate, gelatinised with amyl acetate. It was at one time a nitrocellulose-nitroglycerin powder, containing soluble nitrocellulose and about 30 p.c. nitroglycerin, the small-arm powder being made into graphited cubes of about 1·5 mm. side.

Maxim-Schupphaus powder is an American powder composed of 80 p.c. insoluble nitrocellulose, 19·5 p.c. soluble nitrocellulose, and 0·5 p.c. urea. Another form contains 80 p.c. guncotton, 9 p.c. nitroglycerin, 10 p.c. collodion cotton, and 1 p.c. urea.

The powder used in the cartridges for the Mannlicher-Schoenauer (Austro-Hungarian) rifle is in the form of thin cupped discs, of 2 mm. diameter, lightly graphited, composed of soluble nitrocellulose, with about 1 p.c. of residual solvent. That for the Mauser (German and Turkish) rifle is of similar form and composition, except that a more highly nitrated cotton is used.

The Japanese use a nitrocellulose powder containing both soluble and insoluble nitrocotton, the proportions of which vary according to the size of the gun in which the powder is to be used; the more rapid powders, used for small arms and guns of low calibre, containing more of the highly nitrated cotton. The modern American powders for large guns are nitrocellulose powders of various degrees of nitration (varying between 11·5 and 13 p.c. nitrogen content), in the form of multitubular sticks; and the Russian and Dutch powders, both for small arms and large guns, are nitrocellulose powders containing various proportions of collodion cotton and guncotton.

(2) *Nitrocellulose Powders with Nitrates.*

Schultze powder, invented by Schultze of Potsdam, and now manufactured in England, was one of the earliest sporting smokeless powders. It is a nitrolignin powder.

Hard wood is cut into sheets and punched into grains. The wood grains are purified by boiling with dilute sodium carbonate, by washing with water, and treating with solution of chloride of lime. They are then washed, dried, and immersed in the mixture of strong nitric and sulphuric acids for 2 or 3 hours, with frequent stirring, the acids being kept cool. The nitrated wood is freed from most of the acid in a centrifugal machine, washed with water, boiled with dilute sodium carbonate, and dried. The nitrolignin appears to contain a large quantity of matters soluble in ether-alcohol, and, besides insoluble nitrolignin, some unconverted wood. It is steeped in a solution of potassium and barium nitrates, and dried at a low temperature.

In later powders, wood pulp is used for nitration. The nitrolignin and nitrate mixture is formed into irregular grains, which are treated with a solvent of nitrolignin to gelatinise and harden them. Another form of the powder, *Imperial Schultze*, consists of about 80 p.c. nitrolignin, 10 p.c. barium nitrate, 8 p.c. vaseline, and 2 p.c. of volatile matter. It is less bulky than the older powder, and is said to be quite free from smoke and to leave no residue.

The *modern 'E. C. powders,'* as already explained, belong to this class.

Amberite, as originally patented by Curtis and Andre (Eng. Pat. 11383, 1891), was a mixture of insoluble and soluble nitrocelluloses with nitroglycerin. The mixed nitrocelluloses

were first granulated, and then treated with ether-alcohol, so that only the soluble nitrocellulose was dissolved, and on drying, cemented the grains together and hardened their surface. A small quantity of linseed oil, paraffin, or shellac, was sometimes added as a moderant.

Amberite, as now manufactured by Curtis and Harvey at Tonbridge, contains a mixture of potassium and barium nitrates instead of the nitroglycerin, and a little paraffin. An analysis gave: 13 p.c. guncotton, 59·5 p.c. collodion cotton, 19·5 p.c. barium nitrate with a little potassium nitrate, 6 p.c. paraffin, and 2 p.c. volatile matter.

Cannonite, also made by Curtis and Harvey, is a similar powder to Amberite, containing a higher proportion of nitrocellulose and a smaller proportion of nitrates, together with small quantities of potassium ferrocyanide and lamp-black. Resin was a constituent of the earlier forms.

Poudre pyroxylée is a French sporting powder, containing soluble and insoluble nitrocotton mixed with about 35 p.c. barium and potassium nitrates. The mixture is incorporated with water, ether is then added, and the mixture granulated. The grains are then dried and afterwards glazed by means of an ether spray. *Poudre J.* contains about 83 p.c. guncotton and 17 p.c. potassium dichromate. *B. N. powder* is a French military powder, similar to 'Poudre B,' with the addition of barium and potassium nitrate and a little sodium carbonate.

W. A. powder made by the American Smokeless Powder Co., is a guncotton-nitroglycerin powder with barium and potassium nitrates. It is manufactured in the same way as cordite, but the powder for small arms is cut into short cylinders.

One form of *U.S. Naval powder* is composed of soluble nitrocellulose with barium and potassium nitrates, and a form of *U.S. Army powder* contains insoluble and soluble nitrocellulose, nitroglycerin, metallic nitrates, and a moderant. Some American small-arm powders, besides barium nitrate, contain a small quantity of starch. One form of *Belgian blank ammunition* consisted of small light-coloured grains of soluble and insoluble nitrocotton, with about 25 p.c. of barium nitrate and a little rosin.

(3) *Nitrocellulose-Nitroglycerin Powders.*

Ballistite, the first nitroglycerin-nitrocellulose powder, as patented by Nobel, was a mixture of equal parts of collodion cotton and nitroglycerin with about 10 p.c. camphor. The mixture was first made with an excess of nitroglycerin, which was afterwards removed in a press or centrifugal machine, and the mass then thoroughly incorporated by passing between steam-heated rollers—malaxation, as Nobel termed it.

In this way, nitrocotton was dissolved in the nitroglycerin, and horny, colloidal sheets of varying thickness obtained, which were afterwards cut up into thin squares or cubes. At some factories, benzene was added to assist the incorporation, and afterwards removed by drying the finished product.

Camphor, suggested to Nobel by its use in celluloid, was at first used to reduce the rate of burning, and was also found to facilitate solution of the nitrocellulose. Owing to its slow evaporation from the finished explosive, it led to variable ballistic results being obtained from the explosive, and its use was subsequently abandoned. 1 to 2 p.c. of aniline or diphenylamine is now usually added to ballistite for the purposes of stabilisation.

Ballistite is now manufactured by an improved process invented by Lundholm and Sayers (Eng. Pat. 10376, 1889). The nitrocotton, in the form of fine powder, is suspended in water at a temperature of about 60°, the nitroglycerin, in which the diphenylamine is dissolved, is added and the mixture stirred by means of compressed air. The nitroglycerin gradually displaces the water and dissolves the nitrocotton, and, when the solution is complete, the water is partly drained off and the remainder removed in a centrifugal or by pressure, and the mass allowed to ripen. The paste is then rolled under heavy pressure, between rollers, steam heated to 50°–60° to complete the incorporation and remove the last traces of water. The great advantage of this process is that the dangerous and tedious drying of the guncotton is done away with.

Ballistite is the Service explosive of Italy, and is used not only in small squares, small perforated cylinders, and larger cubes, but also in cords, '*Filite*,' and round flakes cut from the cords. The powders sometimes contain a little mineral jelly. Ballistite is used for certain military purposes in England, and has been adopted by some other countries specially for large guns.

Ballistite is dark-brown in colour, and has an average density of 1·6. It has the consistency of soft horn, and can easily be cut with a knife. It is but little affected by moisture, but is more susceptible to heat than most smokeless powders, the nitroglycerin tending to exude. The grains are frequently coated with graphite. It burns slowly in the open, and is almost entirely smokeless.

Cordite, the English Service propellant, is so named because of its usual cord-like form. For special purposes, however, it is made into tubes, with single or several perforations, and is sometimes used in the form of tape, and in flakes made by slicing cords.

Composition.—Cordite is essentially a mixture of nitroglycerin and guncotton, thoroughly incorporated and gelatinised by means of acetone. The guncotton has a nitrogen content of 12·8–13·1 p.c., and contains not more than 12 p.c. soluble nitrocellulose. A small proportion of vaseline, or the cruder mineral jelly, is the third ingredient.

Mineral jelly was originally added to prevent metallic fouling of the magazine rifles by the bullets, and was also found to improve the regularity of the burning and act as a waterproofing agent.

It was subsequently found that cordite made for blank purposes without mineral jelly was considerably less stable in hot climates than ordinary cordite, and it is now recognised that the mineral jelly contains constituents, olefines and naphthenes, that stabilise the cordite for a prolonged period by combining with the products of decomposition.

The mineral jelly obtained in a particular stage of the distillation of petroleum, used in the manufacture of cordite, is required to have a

flash-point above 204·5°C. (400°F.), and not to be completely melted below 30°. It must be free from acidity and mineral impurities, and have a sp.gr. of not less than 0·87 when melted at 38°.

The guncotton used for the manufacture of cordite usually contains from 10 to 12 p.c. soluble nitrocellulose.

The original cordite, the manufacture of which was commenced at the Royal Gunpowder Factory in 1890, was composed of 58 p.c. nitroglycerin, 37 p.c. guncotton, and 5 p.c. mineral jelly. The composition was the same for small-arms and for the different calibred guns for which it was used, the requisite rate of combustion being obtained by varying the diameter of the cord. Owing to its high nitroglycerin content, this cordite had a high temperature of explosion, and produced considerable erosion in guns of very large calibre, and in 1901 its composition was modified for some purposes. This modified composition, known as '*Cordite M.D.*,' contains 30 p.c. nitroglycerin, 65 p.c. guncotton, and 5 p.c. mineral jelly. The older composition is known as '*Cordite Mark I.*'; both varieties are now in use. Cordite contains practically no moisture, but retains about 0·4–0·6 p.c. of acetone, according to the size of the cords. Cordite M. D., owing to its smaller proportion of nitroglycerin, retains more volatile matter, about 0·5 to 1·5 p.c.

Manufacture: *Drying the guncotton.*—Formerly the guncotton was dried in a loose condition, but it is now loosely compressed into cylinders 3 inches diameter and 4½ inches high, containing about 40 p.c. moisture. Guncotton dust formed in the drying is the great source of danger, and its formation is obviated by the present method. The guncotton cylinders are dried in a stove on wire-gauze trays, by a current of air heated to about 40°, until they contain about 0·5 p.c. moisture. The drying takes from 90 to 100 hours.

Mixing.—The charge of dry guncotton is weighed out into a rubber-lined canvas bag, carried to the nitroglycerin filtering house, and the requisite charge of nitroglycerin, which was at one time weighed out, is measured out from a lead burette through a rubber tube on to the guncotton. The bag is then carried to the mixing house and the contents roughly mixed by hand and rubbed through a copper wire sieve of ½-inch mesh. The product at this stage is known as '*Cordite paste.*'

Incorporating.—Part of the acetone charge is first poured into a kneading machine of the usual type, the machine started, and the cordite paste and the remainder of the acetone, about 20 p.c. in all, gradually added. The mixture is covered to prevent loss of acetone, and the mixture kneaded for 3½ hours. At the end of this time, the charge of mineral jelly is added, and the machine run for another 3½ hours. During the kneading, the acetone gradually dissolves the guncotton and nitroglycerin, and thoroughly incorporates them with the mineral jelly. The product is called '*Cordite dough.*'

Pressing.—The cordite dough is conveyed in barrels to the press house, where it is 'squirted' or pressed by plungers working in cylindrical moulds through a die with one or more holes, according to the diameter of the cord required. A perforated plate, supporting a fine wire gauze diaphragm, is placed above the die to retain mechanical impurities. Three kinds of presses are used at Waltham Abbey—screw presses for the smaller sizes, and hydraulic or combined screw and hydraulic presses for the larger sizes. The smaller-sized cords are wound automatically on to reels as they leave the die, the larger sizes are cut into the required lengths.

The sizes of Service cordite refer to the diameter of the cords in hundredths of an inch. It varies from size 3¾ to size 50; that is, from 0·0375 inch. diameter used in the ·303 Service rifle to 0·5 inch diameter used in heavy guns.

Drying.—The cordite is then placed on the reels, or the larger sizes on trays, on open racks in stoves, heated by steam pipes or by a current of hot air at a temperature of about 40°. The time required for drying varies, according to the diameter of the cord, from 2 to 15 days. The drying is to remove any moisture and the greater part of the acetone, of which about 15 p.c. remains in the pressed cordite.

A process for the recovery of the acetone has been patented by Robertson and Rintoul (Eng. Pat. 25994, 1901), in which the air, containing only a low percentage of acetone, after being saturated with moisture, is led into a scrubbing tower through which a 30 p.c. solution of sodium bisulphite trickles. The acetone is recovered by distillation at a temperature such that the bisulphite is not decomposed and can be used again.

Blending.—The cordite is finally thoroughly blended in order to obtain average uniformity of composition and ballistics. The small-arm cordite is blended by uniformly winding the cords from 10 reels on to one larger reel, and afterwards from six of these ten-stranded reels on to one sixty-stranded reel. The larger sizes are blended by hand, the sticks from the drying-stove trays being placed in boxes and the contents of these blended by combining a few sticks from each box, the operation being repeated.

Testing: *Moisture.*—The residual solvent or moisture is determined on the ground sample, precaution being taken to prevent loss of nitroglycerin. 5 grams of siftings of the same size as those used for the Abel heat test, are heated for 2 hours on a water-bath in an aluminium dish covered with a glass cone, both of specified dimensions (*see* Marshall, J. Soc. Chem. Ind. 1904, 154).

Analysis.—Weigh out 2 grams of very fine siftings into a Soxhlet thimble, and allow to stand covered with ether in the extractor overnight. Extract for 2 hours, then dry the thimble and contents at 50° until the guncotton can be removed to watch glasses. Dry at the same temperature till the *guncotton* is of constant weight. The extracted guncotton may be submitted to the usual tests for guncotton.

Distil off the ether from the extract and dissolve out the nitroglycerin with cold methyl alcohol, filtering the solution. Dissolve any mineral jelly on the filter with ether back into the flask, distil, heat in a water-oven, and suck out any traces of nitroglycerin vapours with an air current. Repeat till the *mineral jelly* is of constant weight. The *nitroglycerin* is usually estimated by difference.

Heat test.—*See* Abel's stability test.

Firing proof for velocity and pressure in a

gun of the standard type for the particular form of cordite (*see* Ballistics of a Propellant).

Properties.—Cordite varies in colour from light to dark brown, according to the colour of the mineral jelly used. Cordite Mark I. has the consistency of hard indiarubber. It is somewhat elastic, and can be readily cut with a knife. Cordite M. D. is considerably harder, being more like horn and more brittle, and can only be cut with difficulty.

Cordite has a slight odour of acetone, and it is poisonous. It is water repellant, and can be kept under water, salt or fresh, for some time without its explosive properties being affected. Even when fired wet from a gun, the ballistics only fall off to the extent due to the evaporation of the water. On prolonged cold storage, the nitroglycerin exudes slightly, but is gradually reabsorbed when the temperature rises. The sp.gr. of cordite Mark I. is about 1·56–1·57, that of cordite M. D. being 1·58–1·59.

Cordite does not ignite very readily, but when once ignited it burns slowly with a strong yellowish flame, which is practically smokeless. A stick becomes pointed at the end as it burns, and the flame can be extinguished by blowing strongly on it. A considerable bulk of cordite can be burned away in the open without any explosion. It only burns explosively when strongly confined: if an ignition of the cordite confined in a wooden box takes place, the cordite does not explode, but burns quietly, and the box is only broken open to allow the gases to escape.

Owing to the difficulty of ignition of cordite, a stronger cap of different composition is necessary to ignite the fine cordite in small-arm ammunition than was required for black powder, and to ensure the ignition of the larger sizes the charge of cordite has to be primed with an ordinary black powder or guncotton 'primer,' which passes on the flame of the igniting 'tube' to the charge.'

Cordite is very insensitive to shock, and cannot be exploded by the passage of a rifle bullet through it.

Exhaustive trials under very varied climatic conditions have proved that the ballistic stability of cordite is very great.

The ballistic power of cordite is very nearly four times that of black powder, owing to the increased volume of gases liberated per unit of weight and the high temperature of the explosion. It can give a pressure, on explosion, of more than 120 tons per square inch, compared with 43 tons, the maximum obtainable with black powder, but in practice the pressure in a gun does not nearly attain this figure (not above 17 tons per square inch) owing to the relatively large size of the gun chamber compared with the volume of the cordite.

The ballistic results of cordite are more influenced by temperature than was the case with black powder, the pressure developed and velocity of the shot being greater with increased temperature, but not to the extent of seriously modifying the shooting under Service conditions. The smaller the size of cordite, the more rapid the explosion, and cordite burns more quickly under high than under low pressures.

The pressure due to cordite is more gradually developed in the gun than was the case with black powder, and is better sustained. The heat of combustion, products of explosion, and other explosion constants for Mark I. cordite were examined, in 1893, by Deering at Woolwich. He worked with an explosion bomb, made of gun-steel, about 1·27 inches in thickness and 108 c.c. capacity. The following are some of the results obtained with a cordite of the composition: loss, 0·24 p.c.; nitroglycerin, 58·55 p.c.; guncotton, 36·11 p.c.; and mineral jelly, 5·10 p.c.; the figures quoted being the averages of a large number of experiments:—

Pressure developed, tons per sq. inch (by crusher gauge)		6·4	13	16
Vol. of perm. gases at 0° and 760 mm., c.c. per gm. cordite		663·7	669·3	671·1
Volume of total ditto ditto		880·7	870·7	869·8
Water formed, gram per gram cordite		0·1757	0·1621	0·1599
Quantity of heat developed, gram degrees C. per gram cordite: water, liquid		1225	1239·1	1242·9
Ditto ditto: water, gaseous		1131	1152·2	1157·2
P.c. comp. perm. gases, vols.	CO_2	25·40	—	28·20
	CO	37·62	—	33·82
	H	17·43	—	18·55
	N	19·55	—	19·09
	CH_4	not dtd.	—	0·34

With the explosion gases at 6·4 tons pressure, Deering calculated the specific heat to be about 0·403, and the temperature of the gases about 2830°; and with a pressure of 7·0 tons, a specific heat of about 0·366 and a temperature of 3120°. The explosion constants of cordite Mark I. and cordite M. D. have also been determined by Robertson, at Waltham Abbey. The following results were obtained with a density of loading of 0·2:—

	Cordite Mark I.	Cordite M. D.
Heat of explosion, calories per gram, at constant vol.: water, gaseous	1156	965
Total gases, c.c. per gram, at 0° at 760 mm.: water, gaseous	871	920
Temperature of explosion, °C.	2663	2374

The larger volume of gaseous products and lower temperature explain why the erosive effect of cordite M. D. is so much less than that of cordite Mark I. The experiments of Nobel have already been referred to.

The erosive effects of cordite are less than those of black powder, and of a different character. With black powder, the surface of the gun is pitted by the corrosive action of the products of combustion, whilst with cordite the surface is smoothly washed away, only near the gun chamber, by the passage of the hot gases between the projectile and the bore, before the inertia of the projectile is overcome. Cordite M. D. gives far less flame than cordite Mark I, when used in rifles or machine guns.

Maxim's powder contains both soluble and insoluble nitrocellulose, mainly insoluble, nitroglycerin, castor oil, and originally an alkaline carbonate. Acetone is the solvent used for gelatinisation. It is made in cylindrical grains or in cords of various diameters.

Axite, made by Kynochs, Ltd., is a guncotton-nitroglycerin powder with special ingredients to reduce the temperature of explosion and decrease metallic fouling, made in the form

of a rail-shaped ribbon. Its ballistics are equal to those of cordite, and are said to be less variable with changes of temperature.

Solenite is an Italian powder containing 40 p.c. insoluble nitrocellulose, 30 p.c. soluble nitrocellulose, and 30 p.c. nitroglycerin gelatinised with acetone.

(4) *Nitrocellulose-Nitro- Derivative Powders.*

Indurite, patented by Munro of the United States (Eng. Pat. 580, 1893), contains 40 p.c. guncotton, freed from lower nitrates by thorough extraction with methyl alcohol, and 60 p.c. mononitrobenzene, with or without oxidising salts. The mixture is rolled into sheets and cut into grains. The grains are treated with hot water or steam, which hardens or indurates it to the consistency of bone: hence the name.

Du Pont powder, patented by Du Pont of the United States (Eng. Pat. 15865, 1893), contains nitrocellulose and nitrobenzene, and sometimes potassium nitrate. The nitrocellulose is agitated in water, the nitrobenzene added, and the mass agitated until the nitrocellulose is dissolved and grains are formed, when the grains are hardened by blowing in steam. In some of the powders, a little nitroresin or nitroturpentine was added as a moderant. Later Du Pont powders contained about 40 p.c. soluble nitrocellulose, 40 p.c. nitroglycerin, and 20 p.c. ammonium picrate, the cylindrical grains being graphited.

Colt's pistol ammunition contains a powder in the form of thin graphited squares, 1 mm. side, consisting of guncotton with about 5 p.c. of dinitrobenzene.

Greener's powder is a nitrocellulose-nitrobenzene powder coloured with lampblack.

Rifleite, manufactured by the Smokeless Powder Co. of Warwick, is a gelatinised nitrocellulose powder containing a small proportion of dinitrotoluene, and the *S.S. powder* of the same company is a similar powder containing a rather large proportion of barium nitrate with a little potassium nitrate and a little wood meal.

Kynoch's smokeless powder is similar in composition to S.S. powder.

Plastomenite is a German powder invented by Güttler, made by incorporating one part of nitrolignin with 5 parts of fused dinitrotoluene and granulating the fused mass. It may also contain barium nitrate.

Some forms of *Norwegian ballistite* contain from 5 to 6 p.c. nitronaphthalene.

Smokeless powders containing picrates, usually ammonium picrate, have been frequently tried, both for sporting and military purposes, but they have been practically abandoned at the present time. Some of the early French military smokeless powders contained picric acid, and at one time a powder containing about 5 p.c. ammonium picrate was tried in the Mauser rifle by Germany.

The American *Peyton powder* was, at one time, a nitrocellulose and nitroglycerin powder containing about 20 p.c. ammonium picrate.

Fulminates.

Although the fulminates of many heavy metals have been prepared, most of them are exceedingly sensitive and too unstable for use in explosives. The mercury salt is the only one in practical use, though *silver fulminate* has been licensed for use in toy fireworks only. Silver fulminate is prepared in a similar manner to mercury fulminate. It is more sensitive to friction and percussion than the mercury compound, and has a greater explosive power.

Mercury fulminate, discovered by Howard in 1800, is produced by the reaction which ensues on mixing together alcohol and a solution of mercury in excess of nitric acid.

In Liebig's process, and Chevalier's modification of it as used in France, the solution of mercury in nitric acid is used cold; in Chandelon's process it is used warm.

Chevalier's process. 3 parts by weight of mercury (300 grams) are dissolved in the cold in 30 parts of nitric acid of 1·34 sp.gr., and the solution is poured into a flask containing 19 parts of alcohol (of 90 p.c. strength). After some minutes an energetic reaction commences, with formation of crystals of mercury fulminate. Towards the end of the operation, two successive additions of 2·38 and 1·58 parts of alcohol are made; the fulminate obtained is thoroughly washed and dried.

The addition of too large a quantity of cold alcohol towards the end of the operation is stated to yield an impure fulminate. The yield by this process varies between 118 and 128 p.c. of the weight of mercury used.

Chandelon's process is the one almost universally used, and the original proportions are usually closely adhered to. 1 part by weight of mercury is dissolved in 10 parts of nitric acid (sp.gr. 1·4) at a gentle heat; the solution, at a temperature of about 55°, is poured into a capacious flask (its capacity must be at least equal to six times the volume of the liquid) containing 8·3 parts of alcohol (of sp.gr. 0·83). The flask is connected by a cork and tube with a stoneware condenser, to recover spirit.

In about a quarter of an hour, the reaction commences with a slight formation of gas bubbles; very soon the liquid boils, and the flask becomes filled with voluminous white vapour. The violence of the action can be checked by adding, as required, a little alcohol; for this purpose the recovered spirit after redistillation with caustic soda can be utilised. If the reaction be too much restrained in this way, the fulminate is likely to contain metallic mercury.

The mercury fulminate is precipitated from the liquid in small greyish-coloured needles. When the action is over, the fulminate is filtered off and washed until free from acidity. The nitric acid liquid, after cooling, does not contain any appreciable quantity of mercury. The calculated yield of fulminate is 142 per 100 of mercury; by this process the mean yield is 125 p.c. mercury fulminate.

A process very similar to the above is employed in this country; the yield of fulminate is about 123 parts per 100 of mercury.

Mercury fulminate is usually light brown-grey in colour. *White fulminate* of mercury is manufactured by adding a little copper and hydrochloric acid or potassium chloride to the solution of mercury nitrate, before pouring it into the alcohol. Solonina (Zeitsch. Ges. Schiess- u. Sprengstoffwesen, 1910, 41, 67). finds that other chlorides have a similar effect, but that the use of hydrochloric acid alone leads to the

formation of a considerable quantity of oxalic acid which contaminates the fulminate. He finds that the purest fulminate results from the addition of cuprous chloride.

Mercury fulminate is sometimes recrystallised from boiling water or from alcohol, but this is not usually found necessary. The best method of purification is to dissolve in pyridine, filter the solution, and precipitate by adding an excess of water. Traces of free mercury can be removed from fulminate by placing it for a few days in a vacuum desiccator.

Angelico (Chem. Zentr. 1901, ii. 404) prepares mercury fulminate by treating a solution of mercury in an excess of dilute nitric acid with a strong aqueous solution of malonic acid and a little sodium nitrite solution. A considerable rise of temperature takes place, with copious evolution of carbonic acid gas, and crystals of fulminate separate out. So far as is known, this process has not been used on the manufacturing scale.

Fulminate is usually stored in linen bags immersed in water. If dry fulminate is required, it is spread out on linen or paper, supported in wooden frames with string-net bottoms, and dried at a temperature not greater than 40°. Passburg of Breslau has devised an apparatus for drying fulminate of mercury in a vacuum. The drying chamber is heated by steam, which can be replaced by cold water when the fulminate is dry. Explosives only burn with difficulty in a vacuum, and there is sufficient vacuous space, with the aid of safety valves, to prevent any damage, should an ignition take place of the quantity of fulminate dried at one time.

Properties.—Commercial mercury fulminate is in the form of small crystals, of white or pale-brown colour. It crystallises in well-defined octahedra, which frequently twin along the major axis.

In a state of purity it crystallises in white silky needles, almost insoluble in cold water, soluble in 130 times its weight of boiling water. It is soluble in pyridine and alcohol. Fulminate may be dissolved to a clear solution in ammonia, and in solutions of potassium cyanide or sodium thiosulphate. A small residue is left from commercial samples, which consists largely of free mercury, but also contains mercury compounds, containing carbon and hydrogen, of uncertain composition. It has a sweetish metallic taste, and is very poisonous.

Its sp.gr. is 4·42 (Berthelot and Vieille). In the dry state it explodes violently by a moderate blow or by slight friction; its sensitiveness is lessened when it is moistened with water. Thus Berthelot states that the presence of 30 p.c. of water prevents the decomposition of the fulminate in fine powder by friction or shock, that with 10 p.c. of water it decomposes without detonation, that with 5 p.c. water only the portion struck detonates. These results were, however, obtained with small quantities of fulminate, and should not be presumed on in manipulating the substance. In small quantities it will burn fiercely without explosion when ignited, and large quantities may be safely destroyed by burning it in a train after mixing with oil. Mercury fulminate, when heated with a large volume of water under pressure, decomposes into metallic mercury and non-explosive mercury compounds of unknown composition. Small quantities may be destroyed by warming with ammonium sulphide.

When only slightly confined, even between sheets of paper, mercury fulminate explodes violently when ignited.

It is detonated by heat; the temperature of explosion is variously stated as 187°, 200°, and 149°. The firing-point, as usual, depends on the rapidity of heating up; ignition takes place at a lower temperature if the explosive be slowly heated than when the heating up is rapid.

It can also be exploded by a spark from an induction coil or by contact with strong sulphuric acid. Fulminate can be exploded by contact with a wire heated to incandescence by means of an electric current, but *in vacuó* only the part actually in contact fires.

The products of its detonation are carbonic oxide, nitrogen, and metallic mercury. Berthelot and Vieille examined them—the fulminate being detonated in an atmosphere of nitrogen—and obtained in five experiments per 1 gram fulminate 234·2 c.c. of gases, consisting of CO_2 0·15 vol., CO 65·70 vols., N 32·26 vols., H 1·89 vols. per 100 vols. gas. This agrees with

$$HgC_2N_2O_2 = 2CO + 2N + Hg,$$

requiring 235·6 c.c. From these results and from an estimation of the mercury, they obtain for the composition by weight of mercury fulminate, C 8·35 p.c., Hg 71·30 p.c., N 9·60 p.c., O 11·05 p.c., H 0·04 p.c., total 100·34, every constituent having been estimated. This confirms the accepted formula $HgC_2N_2O_2$, requiring C 8·45 p.c., Hg 70·42 p.c., N 9·86 p.c., O 11·27 p.c. The fulminate analysed contained a trace of metallic mercury.

The decomposition $HgC_2N_2O_2$ into

$$2CO + 2N + Hg$$

disengages +114·5 Calories (kgm.-degrees) of heat at constant pressure per 284 grams fulminate, the mercury supposed liquid; for mercury gaseous, +99·1 Cals.; or per 1 kgm. fulminate, 403 Cals. and 349 Cals. respectively. Mercury fulminate is an endothermic substance; in its formation from its elements there is absorption of heat, −62·9 Cals. per 284 grams, or −221·5 Cals. per 1 kgm.

The pressure produced by the detonation of mercury fulminate in a space entirely filled by it has been estimated by Berthelot and Vieille in the crusher-gauge apparatus of the former; they find it to be more than twice that of nitroglycerin, and about three times that of guncotton, detonated in spaces filled by them (but including the interstitial air of the guncotton). They attribute the power of mercury fulminate in effecting detonation to the greatness of this pressure, coupled with its sudden development (Berthelot and Vieille, Annalen, [21] 569, 1880).

The main factor causing the detonative character of the explosion of mercury fulminate, is, perhaps, the extreme rapidity of the explosion, which is further helped by the high density of the explosive. The effects of the detonation of fulminate and fulminate compositions are always quite local. The sharpness of the explosion is also no doubt connected with the

fact that the products of detonation do not undergo dissociation, and so the explosive reaction is not prolonged by this phenomenon, as is usually the case.

The larger the crystals of fulminate, the more easily can it be detonated and the greater the explosive effect: for this reason, brown or grey fulminate is slightly more powerful than white.

Testing: *Microscope.*—The crystals should be well defined, of uniform size, and free from visible impurities. Metallic mercury can sometimes be detected.

Total mercury is estimated by dissolving the sample in strong ammonia or a solution of potassium cyanide, precipitating with ammonium sulphide, and weighing the mercury sulphide as usual. It may also be estimated by electrolytic deposition on copper. The sample should preferably be dried in an atmosphere saturated with mercury vapour to prevent loss of free mercury. Commercial samples generally contain about 70·5 p.c. Hg.

Free mercury is determined by dissolving the sample in 0·880 ammonia or other solvent filtering and washing the residue, and determining the mercury in it as usual. As already mentioned, this residue also contains some mercury compounds; an idea of the quantity of free mercury can be got by examining the residue on the paper microscopically before dissolving in acid.

Oxalate is determined in the filtrate from the mercury sulphide in the total mercury estimation, by adding NH_4Cl and $CaCl_2$.

Carbon and nitrogen may be estimated by a careful combustion, if the fulminate is mixed with a large excess of copper oxide. The mercury is absorbed by gold leaf placed in the calcium chloride tube.

Explosive power is found by firing in lead blocks. 20 grains are fired, electrically, in a cylindrical lead block 6 inches high and 4 inches in diameter, with an axial cylindrical hole 0·25 inch in diameter and 3 inches deep. The enlargement of the cavity formed, measured by running in water from a burette, is an index of the explosive power, as compared with that of standard samples.

Fulminate Compositions.

Mercury fulminate is used in detonators, and is the active ingredient in igniting and detonating mixtures, its value depending on its extreme sensitiveness to friction and percussion.

Igniting mixtures. Mercury fulminate is too rapid in its action to be used alone. On firing a train of fulminate covered with gunpowder or cordite, the latter are simply dispersed without being ignited. If the fulminate be mixed with a little potassium chlorate, the rate of burning is decreased, and the temperature and flame increased by the combustion of the carbonic oxide, and the powders are ignited. The explosion with potassium chlorate may be represented by:

$$3HgC_2N_2O_2+2KClO_3=2KCl+3Hg+6CO_2+3N_2$$

A mixture of 22·3 p.c. potassium chlorate and 77·7 p.c. mercury fulminate, *i.e.* in the proportion required for the oxidation of the carbon to carbon dioxide, gives by its explosion 706 cals. (mercury, liquid) or 663 cals. (mercury, gaseous) per 1 kgm. of mixture. The volume of gases (at 0° and 760 mm.) produced is 183 litres per 1 kgm.—less than with the fulminate alone; the theoretical pressure is very near that of pure fulminate. The chlorate renders the mixture very sensitive (Berthelot).

Percussion caps were invented by Egg in 1815. The cap shells are small closed cylinders usually of pure copper. In the early caps, pure fulminate was used agglomerated by means of wax or an aqueous solution of gum.

In later igniting compositions, mercury fulminate and potassium chlorate were mixed with other combustible substances, such as antimony sulphide, sulphur, and mealed powder, to increase the size of the flame and ensure ignition of the powder. Powdered glass is frequently added to increase the frictional surfaces and sensitiveness of the composition. The best igniting composition for any particular composition and form of propellant has largely to be found by experiment.

A cap composition must not be too slow nor too rapid in its rate of burning. If too slow, much of the heat of combustion may be conveyed to the metal parts and irregular ignition of the propellant or even miss-fires may occur; and, on the other hand, if too rapid the charge of propellant is disturbed and uneven ignition and irregular firing results are obtained. There should be a certain proportion of solid ingredients of high specific heat in the combustion products, in order to make ignition certain. To secure regularity of ignition, the ingredients of the composition should be of even size and well mixed.

Aluminium powder has been suggested by Brownsdon (Eng. Pat. 23366, 1904) as an addition to increase the strength of cap composition, the metal being either mixed with the other ingredients or pressed in a layer on the surface. Zieger (Eng. Pat. 14583, 1900) suggests barium nitrate, with a little barium carbonate, as a substitute for the potassium chlorate: the products are said to act less corrosively on the gun-barrel, and the carbonate is said to give stability to the mixture.

For black gunpowder, the English Service cap composition was a mixture of 37·5 p.c. mercury fulminate, 37·5 p.c. potassium chlorate, and 25 p.c. antimony sulphide, with in some cases 12·5 p.c. ground glass, the charge being 0·22 to 0·25 grain per cap. A mixture of similar composition was used by most other countries.

For smokeless powders, which are more difficult of ignition, a slower mixture with a longer flame is necessary. The Service composition for cordite small-arm ammunition is composed of 19·05 p.c. mercury fulminate, 33·33 p.c. potassium chlorate, 42·86 p.c. antimony sulphide, and 2·38 p.c. each sulphur and mealed powder. The charge per cap is 0·6 grain.

Mixing cap compositions. The ingredients of cap compositions were formerly mixed in a wooden mortar for some hours, after wetting with an aqueous solution of gum arabic or an alcoholic solution of gum benzoin, or were mixed by hand on paper and afterwards sifted. The ingredients are now usually mixed dry. In England and France, a so-called 'jelly bag' is used: this is a conical silk bag with rows of

indiarubber rings strung on cords passing from top to bottom. The contents are mixed together by working the bag up and down by means of a cord fastened to the apex of the bag. The mixing only takes a few minutes. In Germany, a similar principle is used, but the mixer is saucer-shaped and contains indiarubber balls.

Charging the caps.—At one time the caps were charged with the wet composition by hand, but now the charging is always done by a machine. The composition in the cap shells is compressed and then covered with shellac varnish or a tinfoil disc, or sometimes both.

Proof.—The usual proof of caps comprises the microscopic and analytical examination of the composition, photographing the flash and a firing proof when made up into cartridges. In special examinations, determinations are made of the total heat of combustion, temperature, and duration of the flash, the volume of gaseous products and their relation to the solid product of combustion, &c. (For details, *see* papers by Brownsdon, J. Soc. Chem. Ind. 1905, 381; and Borland, *ibid.* 1906, 241.)

Detonators may be fired electrically or by the flame from a fuse, and the construction varies accordingly, but the detonating composition is contained in what are practically long percussion caps made generally of copper.

The charge, as in the case of caps, was at one time pure fulminate, and is at the present time in many Service detonators, but a mixture of fulminate with potassium chlorate, and sometimes other ingredients, such as guncotton, is now usually used in industrial detonators. The mixtures usually contain about 85 p.c. mercury fulminate. The detonators are charged and the charge compressed as with caps, except that detonators are usually compressed singly, owing to the strength of the charge. A pressure of about 4000 lbs. per square inch is used, giving the fulminate or mixture a density of 2·8. The ingredients should be even in size and well mixed to act efficiently.

The following detonators are used:—

Description No.	1	2	3	4	5	6	7	8
Charge, grams .	0·3	0·4	0·54	0·65	0·8	1·0	1·5	2

They vary in length, from 16 to 45 mm., and in diameter from 5·5 to 6·8 mm.

To obtain the full effect from a detonating explosive, a detonator of sufficient power is necessary. A No. 3 detonator is sufficient for ordinary dynamite, but for the modern safety explosives, such as those of the ammonium nitrate class, at least a No. 6 detonator is necessary for effective detonation of the explosive.

As a detonating composition for high explosives, which can be fired with safety in shells, Maxim (Eng. Pat. 18682, 1894) proposes a mixture of 75 to 85 p.c. of mercury fulminate with 15 to 25 p.c. of a blasting gelatin composed of 75 to 85 p.c. of nitroglycerin and 15–25 p.c. of collodion cotton. The admixture is aided by the use of acetone, and to decrease the sensitiveness the mixture is sometimes made of a spongy nature by blowing air through it whilst it is in a syrupy condition, or nitrobenzene may be added.

Other igniting and detonating compositions. Many mixtures, frequently not containing mercury fulminate, have been from time to time suggested. The drawback to fulminate cap compositions is that the mercury in the combustion products attacks the metal of the cartridge cases, causing them to crack and be unfit for further recharging. Early mixtures containing guncotton and potassium chlorate, lead picrate, &c., were not very successful. Mixtures of mercury or lead thiocyanate with potassium chlorate, and of mercury or lead chromate, mercury fulminate, antimony sulphide, and powdered glass have been proved efficient with certain sporting powders. A mixture of 82·8 p.c. of mercury fulminate and 17·2 p.c. of ammonium perchlorate was suggested by Alvisi (U.S. Pat. 707493, 1902). It was proposed by Bielefeldt (Eng. Pat. 20133, 1900) to substitute all or part of the mercury fulminate in detonating composition by picric acid, nitronaphthalene, nitrocellulose, &c. With safety explosives, he also suggested the addition of aluminium nitrate. Wöhler (Eng. Pat. 21065, 1900) proposed the use of high nitro derivatives, such as trinitrotoluene; and Gehre (Eng. Pat. 19402, 1905) suggested di- or tri-nitromesitylene, and di- or tri- nitropseudocumene. A little fulminate is necessary to ensure ignition, but with trinitrotoluene not more than one-tenth of the usual quantity. Trinitrotoluene detonators are very largely used in Germany, and the Rheinisch-Westfälische Gesellschaft have patented the use of tetranitromethylaniline, or 'Tetryl' (Eng. Pat. 13340, 1905).

As substitutes for mercury fulminate, Angeli (Fr. Pat. 327892, 1902) proposed the barium, strontium, or calcium salts of the hydroxamic acids; Wöhler (Ger. Pat. 196824, 1907) proposed the nitrides of silver, mercury, or other heavy metal: it is claimed that a smaller quantity of these substances is necessary. Hyronimus (Eng. Pat. 1819, 1908) suggested the use of lead nitride.

Mixtures, without fulminate, containing aluminium, have been proposed by Führer (Eng. Pat. 2755, 1901, and 24812, 1902), Bielefeldt (Eng. Pat. 7148, 1901), and von Dahmen (U.S. Pat. 702357, 1902), but these mixtures require very strong confinement to be effective; the Westfälisch-Anhaltische Sprengstoff Actien-Gesellschaft have patented mixtures without fulminate, containing potassium chlorate with mono-, di-, or tri-nitrocresol, &c.; and Bielefeldt (Eng. Pat. 23889, 1901) suggests a mixture of potassium chlorate with trinitronaphthalene.

Efficiency.—Detonants have, by their effect when detonated on a lead plate, been placed in the following order of efficiency as regards their value as initial detonants for other explosives, by Wöhler and Mauer (Zeitsch. Ges. Schiess- u. Sprengstoffwesen, 1907, 265): silver azoimide, mercury fulminate, trimercuraldehyde and a perchlorate, trimercuraldehyde and a chlorate, diazobenzene nitrate, nitrogen sulphide, sodium fulminate, and mercury nitromethane.

Other Explosive Compounds.

Nitrostarch. Braconnot and Pelouze first nitrated starch at the same time as cellulose, the explosive product, like nitrocellulose, being originally called 'xyloïdin.' Attempts to use nitrostarch, from time to time, for explosive work failed, partly owing to the instability of

the product, and partly because the product had a considerably smaller nitrogen content than nitrocellulose.

Braconnot and Pelouze carried out the nitration with nitric acid *alone*. Uchatius first used a mixture of nitric and sulphuric acids. In his process the starch was not added directly to the acid mixture, as it clotted together and resisted nitration, but was dissolved in 8 parts of cooled fuming nitric acid and the syrupy solution poured, with stirring, into 16 parts of concentrated sulphuric acid. The mixture was allowed to stand for 12 hours, washed, boiled with a solution of sodium carbonate, and dried at 60°.

The product was a white powder insoluble in water and alcohol, but soluble in ether. It was very hygroscopic and readily decomposed spontaneously, doubtless because of insufficient purification. It ignited at about 175°, and was very explosive.

Later, in America, Volney succeeded in nitrating starch directly in cold mixed acids by using a special stirring apparatus.

The Actien-Gesellschaft Dynamit Nobel, in 1891, patented the use of nitrostarch in smokeless powders (Eng. Pat. 6129, 1891), and prepared it on the manufacturing scale. The method of preparation is similar to that of Uchatius. The well-dried starch is first dissolved in 10 parts of nitric acid, of 1·5 sp.gr., in a special apparatus of lead, in which the mixture is well circulated by means of a paddle stirrer, and kept well cooled by means of inner and outer water-jackets. When all the starch is dissolved, the solution is introduced as a spray from an 'atomiser' into five times its weight of mixed acids, as a rule waste acids from nitroglycerin manufacture, containing 70 p.c. H_2SO_4, 10 p.c. HNO_3, and 20 p.c. H_2O. The nitrostarch is precipitated as a fine powder, and is retained on a filter of guncotton between two perforated plates, when the waste acids are run off from the bottom of the vessel. The acid is pressed out, and the cake of nitrostarch stirred in water until neutral. The product is treated for 24 hours with a 5 p.c. solution of sodium carbonate, and finally stabilised by soaking in a solution of aniline. The finished cake contains about 23 p.c. water and 1 p.c. aniline. The nitrostarch so obtained is a mixture of mono-, di-, and tetra-nitrates, when related to $C_{12}H_{20}O_{10}$ as the molecule of starch—that is, up to and mainly $C_{12}H_{16}O_6(NO_3)_4$, containing 11·11 p.c. nitrogen. It is readily soluble in nitroglycerin, even in the cold, and forms gelatinous to waxy solids when sufficient of the nitrostarch is added.

The penta- and hexa- nitrostarches, on the same basis, have been prepared by Mühlhäusen (Dingl. poly. J. 1892, 137). *Pentanitrostarch* $C_{12}H_{15}O_5(NO_3)_5$, containing 12·75 p.c. nitrogen, was prepared by adding dry starch to twenty times its weight of a mixture of 1 part of nitric acid, sp.gr. 1·5, and 3 parts of sulphuric acid, sp.gr. 1·8. The product, stabilised in the usual way, was freed from the tetranitrate by dissolving in ether-alcohol and distilling off the ether. The tetranitrate remained in solution in the alcohol, and the pentanitrate was precipitated. *Hexanitrostarch* $C_{12}H_{14}O_4(NO_3)_6$, containing 14·14 p.c. nitrogen, was prepared, mixed with the pentanitrate, by dissolving dry starch in ten times its weight of nitric acid, sp.gr. 1·5, standing 24 hours, and pouring the solution into five times its weight of sulphuric acid, sp.gr. 1·77.

A nitrostarch containing 16·5 p.c. nitrogen, corresponding to an *octonitrate* of the composition $C_{12}H_{12}O_2(NO_3)_8$, was prepared by Hough in the United States in 1904 (U. S. Pat. 751076, 1904) by injecting dried maize starch below the surface of an acid mixture consisting of 3 parts of strong nitric acid, 2 parts of strong sulphuric acid, and sufficient Nordhausen sulphuric acid, containing 40 p.c. SO_3, to give an excess of 2 to 3 p.c. of unhydrated SO_3. The temperature is kept at 7° to 10°, and Nordhausen acid is added during the nitration to keep up the strength of the mixture. The nitrated starch is filtered off, washed, and treated with hot dilute ammonia to dissolve out lower nitrates and stabilise the product. The final product is an orange-coloured powder, soluble in ether-alcohol. Subsequently, Holmes (U. S. Pat. 779422, 1905) stabilised the product by dissolving in a mixture of alcohol and acetone, and then evaporating off the acetone. The impurities and lower nitrates remain in solution in the alcohol.

This nitrostarch is used in several American smokeless powders, and was also for a time tried as a constituent in a U.S. Service powder.

The production of so highly nitrated a starch as claimed by Hough has been questioned by Berl and Butler (Zeitsch. ges. Schiess. u. Sprengstoffw. 1910, 82). Using Hough's method, they failed to obtain a product with a higher nitrogen content than 13·44 p.c.

Nitrodextrin, prepared similarly to nitrostarch, has been proposed for use with ammonium nitrate in safety explosives, mixed with a little resin.

Nitromannite or Nitromannitol, a nitric ester $C_6H_8(NO_3)_6$, prepared by the action of the usual mixed acids on the hexahydric alcohol mannitol, extracted from manna, the dried sap of the manna ash (*Fraxinus Ornus*) (Linn.). The nitrated product, after being well washed, and dried at 40°, crystallises from ether or alcohol in needle-shaped crystals, which are insoluble in water. It is a very sensitive and highly explosive compound, exploding at about 300°, and has been suggested as a substitute for mercury fulminate. It is more sensitive to friction and shock than nitroglycerin, and nearly as powerful and local in its effects as fulminate. It is stable when thoroughly purified, but this purification is difficult to obtain on the large scale, and the product is usually very liable to spontaneous decomposition.

Nitrosugars. Nitrosaccharose, nitro-cane sugar, or 'fulminating sugar,' was first obtained by Schönbein, by nitrating cane sugar with a mixture of 1 part of strong nitric acid and 2 parts of strong sulphuric acid at 12°, washing, and drying. It is a white, amorphous powder, soluble in water, alcohol, and ether. On gently heating, it softens, and can be kneaded, but on strongly heating, it explodes violently. It is very sensitive and has been proposed for use in percussion caps. It is, however, deliquescent, and, as prepared up to the present, very unstable. *Nitrolactose* is similar to nitrosaccharose, but can be crystallised from its solution in alcohol or ether. It has similar violently explosive properties, and is equally sensitive and unstable. *Nitroglucose*, with vegetable fibre and potassium

chlorate and nitrate, is a constituent of *Keil's explosive*, and solid and liquid nitro products, obtained from molasses, have also been proposed.

Other nitro explosives, prepared by the nitration of a great variety of organic substances, such as wood, flax, hemp, jute, gelatin, resin, coal, &c., have been prepared, and several have been already mentioned as constituents of various explosive mixtures.

Amino, and amino-nitro explosive compounds. Ammonium nitrate may be considered as the simplest of the amino-nitro compounds. Glycocoll nitrate, the nitrate of aminoacetic acid, has been used in a propellant, and good results obtained. Its explosion may be represented by:

$$CH_3(NH_2)\cdot COOH\cdot HNO_3 = 3H_2O + 2CO + N_2,$$

and its explosion constants have been compared with those of picric acid by de la Roque (Rev. de Chem. indus. 11, 5). The Westfälish-Anhalt-Sprengstoff. A. G. (Ger. Pat. 203190, 1907) suggested the dinitrodialkylamides for use in explosives. The nitrates of the aromatic amines, like aniline nitrate, are used as constituents (for example, Ceipek (Fr. Pat. 341021, 1904) mixes the latter with ammonium nitrate), but they do not contain sufficient oxygen to form explosives by themselves. Hermann (Ger. Pat. 176072, 1905) proposes condensation products of formaldehyde and the aromatic amines.

Picramic acid and the picramates, and the corresponding reduction products of trinitrocresol, were proposed by Turpin in potassium nitrate mixtures (Fr. Pat. 185034, 1887). Claessen (Fr. Pat. 355695, 1905) proposed tetranitromethylaniline and the ethyl compound, as detonating explosives, and Will (U.S. Pat. 827768, 1906) uses the same compound mixed with mercury fulminate. Nitramines of the anthraquinone series of various degrees of nitration and explosibility have been suggested by Scholl (Ber. 1904, 4427), and von Schroetter (Eng. Pat. 8156, 1907) proposed hexanitrodiphenylamine and its salts, alone or in mixtures. Nitro derivatives of the condensation products obtained by heating primary aromatic amines with oxalic acid, and the nitro derivatives of aromatic diamines, such as pentanitrodimethylmetaphenylenediamine, have been claimed by the Soc. Anon. d'Explosifs, &c. (Fr. Pat. 391106 and 391107, 1907). *Tetralit*, a Spanish high explosive used in shells, is said to be prepared from tetranitromethylamine (Zeitsch. Ges. Schiess- u. Sprengstoffw. 1908, 308), and the Rheinsch. Westfälisch. Gessells. use tetranitromethylaniline in detonators under the name of *Tetryl*.

Diazo explosive compounds. All the diazo derivatives are very sensitive explosive compounds. '*Chromate de benzine diazotée*' $C_6H_5N_2HCrO_4$ is one of a class of explosive compounds proposed as detonants by Caro and Griess (Eng. Pat. 1956, 1866). The diazo compounds generally are too sensitive and highly dangerous to be used in practical explosives.

Azo compounds. The azo compounds are more stable than the diazo compounds. They do not form explosives in themselves, but have been proposed in mixtures. For example, Girard (Fr. Pat. 349635, 1904) uses azobenzene mixed with dinitrotoluene or picric acid in chlorate and ammonium nitrate mixtures, in order to lower the melting-point of the nitro compound, and effect incorporation at a lower temperature.

Hydrazines. Hydrazine chlorate and perchlorate have been prepared by Salvadori (Gazz. chim. ital. 1907, ii. 32): they are highly explosive and sensitive compounds, the perchlorate being the more stable.

Hydrazoic acid, or azoimide HN_3, is one of the most explosive substances known. It is a volatile liquid, the vapour of which detonates on contact with a flame. The aqueous solution of the acid forms metallic salts; those of the heavy metals being extremely explosive. With ammonia it forms a white crystalline solid $HN_3\cdot NH_3$, which is less explosive. It burns away rapidly but not explosively, unless confined.

Azides. The use of the nitrides of the heavy metals has been referred to under detonating compositions.

The explosive properties of the *nitrogen halogen compounds* are well known, but these compounds are unsuitable for practical explosives.

Acetylene compounds. Many of the compounds formed by the action of acetylene on metallic oxides and salts are violent explosives, and have been proposed as detonating explosives. The white solid obtained by passing acetylene into an acid solution of silver nitrate has been claimed by the Société Anon. Dynam. Nobel (Fr. Pat. 321285, 1902) as a substitute for mercury fulminate in chlorate detonating mixtures, and that obtained from an ammoniacal solution of mercury nitrate has been proposed by Venier (Fr. Pat. 364461, 1906) for a similar purpose.

Safety Explosives.

Prior to about 1880, black gunpowder and dynamite were almost the only explosives used in mines and quarries; the former for mining soft coal or obtaining large blocks of rock, the latter for the harder materials and where shattering effects were desired. At the present time, although gunpowder is used in this country to the extent of more than half the total weight of mining explosives, kieselguhr dynamite has been largely displaced by blasting gelatin, and a large variety of other explosives have come into use, more especially the so-called 'safety explosives' used in 'fiery' coal-mines. The use of gunpowder in these mines is everywhere prohibited.

The following table, taken from the 34th Annual Report of H.M. Inspector of Explosives, gives the amount of different explosives used in mines and quarries in Great Britain in 1909:—

Explosive	Quantity used, lbs.	P.c. of total
Permitted explosives .	8,502,232	28·3
Gunpowder . . .	17,595,475	58·5
Gelignite	3,085,529	10·2
Blasting gelatin and gelatin dynamite . .	616,436	2·0
Cheddite . . .	123,531	0·4
Dynamite . . .	117,260	0·4
Various . . .	51,424	0·2
Total .	30,091,887	100·0

Of the 'permitted explosives,' those most used, in order of quantity, were: bobbinite, arkite, monobel, ammonite, samsonite, saxonite, rippite, roburite, westfalite, bellite, carbonite, stowite, Faversham powder, ammonal, albionite, &c.

Owing to an ever-increasing number of coal-mine explosions, due to the ignition of fire damp or dust by the firing of shots, the British Government appointed a Commission, which recommended that the explosive should be surrounded by a jacket of water, but no attempt was made to devise a safety explosive. Subsequent to the English Commission, several of the Governments on the Continent also appointed Commissions, but the factors which render an explosive safe to use in contact with inflammable mixtures were not definitely settled, and even now they are not known with certainty. It has been found impossible to devise an explosive that is absolutely safe under all conditions, and at the present time there is, in this country, no special definition of a 'safety explosive,' except that it must pass the Home Office tests and be placed on the 'permitted list.'

According to the French Commission, in 1888, the factors determining the ignition of inflammable mixtures are the temperature of explosion of the explosive and the duration of the flash. They found that a mixture of marsh gas and air ignited at 650°, but that at this temperature the ignition was delayed ten seconds, and a much higher temperature was permissible, if of short duration. A safety explosive had to fulfil the conditions that the products of explosion were free from inflammable substances, and that the calculated temperature of explosion should be below 1500°.

This temperature limit cannot, however, be rigidly applied; for 'carbonite,' the first safety explosive, and at the present time one of the safest, had a temperature of explosion well above this limit. According to Bichel, the inventor of carbonite, the calculated temperature of the explosion is of no value in determining safety, but the maximum temperature of the products of combustion, the length and duration of the flame, and the velocity of detonation, are the determining factors. The amount of the explosive used and the physical and chemical nature of the products of combustion, for example, the proportion of incandescent solid particles, are of great importance (Glückauf, 1904, 35).

The Prussian Commission came to the conclusion that the quicker the explosion, the greater the safety; consequently, that kieselguhr dynamite and guncotton were safe, and that fulminate detonators could not ignite pit gas. But this view is no longer held to be true in all cases; for 'bobbinite,' a slow black powder mixture, is one of the safest and most extensively used safety explosives, whilst blasting gelatin is not safe.

The Austrian Committee defined a safety explosive as one that gives a short, but not bright, flame, and one that passes the usual gallery tests. Von Lauer, in Austria, stated that bore-hole shots that have done their work never ignite pit gas, and that the risk arises from blown-out shots and fissured coal, but this contention has not held good in all cases. Guttmann considered that the risk of a blown-out shot is frequently due to the rapidity of the explosion being sufficient to ignite the gas mixture, owing to the heat produced by the compression and friction set up in the atmosphere by the explosion gases.

Testing galleries.—The question as to whether explosives are suitable for use in fiery mines is now chiefly decided by submitting them to a practical test, which is intended to simulate, more or less, the conditions of use in these mines. The exact nature of the test varies in different countries, and the severity of the test has, from time to time, been increased as the factors determining safety have become better understood, and the manufacture of safety explosives consequently become more perfected. Explosives at one time 'permitted' are occasionally removed from the list, as the conditions of test are made more stringent.

The test consists in firing a number of shots under definite conditions into an explosive mixture contained in a long gallery, the explosive passing the test when no explosion occurs. Most countries have one or more official testing stations, and many manufacturers of explosives have their own testing galleries.

A testing gallery, based on a private one belonging to some north-country private manufacturers, was established at Woolwich in consequence of the Coal-Mines Regulation Act, 1896, to test explosives proposed for use in coal-mines. Those that pass this test are put on the list of *'permitted explosives,'* which indicates, not that they are absolutely safe under all conditions of use, but that they are safer than those not on the list. It is, indeed, recognised that all explosives, used under certain conditions and in sufficient quantity, will ignite mixtures of pit gas or coal-dust and air.

In testing, a given weight of the explosive is fired from a gun into a mixture of 85 p.c. air and 15 p.c. coal gas. The shot is 'stemmed' with a definite length of dried pottery clay. These conditions at Woolwich are not intended to exactly imitate the actual conditions obtaining in a fiery mine, but rather to give a severe test which can be uniformly reproduced at any time. It is for this reason that coal-dust is not employed in the Woolwich test.

The Woolwich testing gallery is an iron tube 2 feet 6 inches in diameter and 28 feet in length, with seven safety-valve orifices at equal intervals along the top of the tube, to allow the escape of the gas following an explosion. The shot is fired from a gun at a definite angle with the roof. Such a weight of the explosive is fired as is equivalent in strength to 4 ozs. of dynamite No. 1. The charge was determined previous to 1900 by finding the weights necessary to give equal enlargements in the lead-block test, but since that time the relative strengths of the various explosives has been measured by a ballistic pendulum test, which has been found to give more accurate results. One of the guns is charged with the explosive and fired from a fixed distance into the muzzle of a 5-ton mortar of 13-inch calibre suspended in an iron framework from an overhead beam. The swing of the mortar gives a measure of the strength of the explosive.

If the gas mixture does not fire in 20 shots, 10 shots with 12 inches' stemming and 10 shots

with 9 inches' stemming, no explosive being left unconsumed, the explosive is considered safe. The size of detonator and nature of the wrapping to be used with the explosive are defined, as these are found to materially affect the results. For instance, explosives containing sulphur are much less safe in a lead alloy case than in a paper wrapper.

On the Continent, similar testing stations exist. The galleries are long wooden or iron tubes, round or oval in section, but usually considerably larger in section than the Woolwich gallery. The galleries vary in sensitiveness according to their diameter, material, and situation; and the results obtained at one gallery are not directly comparable with those obtained at others. A particular gallery will also give irregular results on certain days, for reasons that have not been explained, and results obtained on these days have to be neglected. The explosive mixture generally used is prepared with natural pit gas, but occasionally artificially prepared methane, coal gas, or even benzene vapour is used, and usually coal-dust is suspended in the explosion mixture. Coal-dust is said not to increase the sensitiveness of the mixtures, but causes the ignition to be more violent and therefore more visible. Beyling showed experimentally (Glückauf, 1908, 1717) that all explosives ignite either coal-dust or a gas mixture more readily than a combination of the two, and in Germany safety explosives are not now tested, as formerly, in a gas mixture containing coal-dust, but in fire-damp (8 to 9 p.c.) and coal-dust mixtures separately. The cannons used vary in bore, and it has been found that the narrower the bore of the cannon, the easier the ignition.

The general method in use is to find the *charge-limité*, or maximum charge of the explosive which, in a series of 10 shots, just fails to fire the explosive mixture, the charge being unstemmed.

The English and Continental systems give very different results, and many explosives passed by the one are condemned by the other.

Composition.—By far the greater number of safety explosives are either nitroglycerin mixtures or ammonium nitrate mixtures. Sometimes the mixtures contain both ammonium nitrate and nitroglycerin, so as to combine the advantages of the two types. Some black powder and chlorate and perchlorate mixtures are also used.

The nitroglycerin explosives, containing a little nitrocotton to gelatinise them, have a high charging density, are readily detonated, and are waterproof. The latter quality enables them to be used in damp or wet bore holes. They are plastic and can be well rammed into the bore holes, thus assuring a maximum effect. They are specially useful in blasting the harder materials. The safety of these explosives varies inversely with the proportion of nitroglycerin, and the maximum permissible is about 30 p.c. The nitroglycerin explosives are not so safe against percussion, such as an accidental blow, or too hard ramming, as the ammonium nitrate explosives; and when so ignited not only does the whole cartridge explode, but the explosion may be communicated to the adjacent cartridges. Another drawback is their liability to freeze.

The ammonium nitrate explosives are very safe, because of the large amount of water contained in the products of explosion, but they are difficult to detonate completely, and usually their hygroscopic nature necessitates the use of a waterproof wrapper. They are so difficult to ignite and so insensitive to percussion, that their transport is quite safe, but their charging density is low and their effect less than that of the nitroglycerin explosives. When ammonium nitrate explosives do fire by percussion, only that portion actually struck is ignited. They necessitate the use of large bore holes, and are consequently best adapted for blasting soft materials. Ammonium nitrate itself is quite safe in any quantity, and the safety of mixtures prepared with it depends on the nature and proportion of the combustible material.

Ammonium nitrate explosives containing a small percentage of nitrocellulose, have been thought, especially in Austria, to be amongst the safest, but they are not permitted in this country. The reason for this is that they are liable to slowly decompose and become acid, and the liberated acid and ammonia attack and decompose the nitrocellulose.

Both Dautriche and Taffanel have established that, by the addition of potassium nitrate to safety explosives, the factor of safety in pit gas mixtures is considerably increased, whether the temperature of explosion be high or low. The heat of combustion is considerably lowered, whilst the explosive force is not appreciably diminished (Taffanel, Zeitsch. Ges. Schiess- u. Sprengstoffw. 1910, 305, &c.).

Safety ingredients.—In safety explosives, the ingredients are so proportioned that the carbon is mainly converted into carbon monoxide. This reduces the temperature of the explosion without sensibly diminishing the explosive force, owing to the increased volume of gases produced. The principle of safety explosives is, further, so to arrange the nature and proportion of the ingredients that a sufficient volume of non-inflammable gas, such as water vapour, carbon dioxide, nitrogen, ammonia, &c., is produced to dilute the carbon monoxide and prevent its contact with the air until its temperature has fallen below the ignition-point.

As already mentioned, the first suggested remedy for the prevention of the ignition of fire damp was to surround the cartridge with a water-jacket. Subsequently it was found that tamping the explosive with wet moss, sand, or clay added considerably to the safety; tamping even with only 1 inch of dry sand was shown by Guttmann to double the safety.

The use of wet tamping materials led to the use of salts containing large quantities of water of crystallisation, such as sodium carbonate and magnesium sulphate, or salts which liberate much water at the temperature of explosion, such as ammonium oxalate.

A large percentage of sodium carbonate is used in 'wetter dynamite' and 'Grisoutine,' and ammonium oxalate in 'securite.' Magnesium sulphate has not been much used because of its effect on the miners.

Another class of additions is salts which dissociate and absorb heat at the temperature of explosion. Examples of this class are the potassium dichromate in 'dahmenite'

potassium permanganate in 'roburite,' and ammonium chloride in 'antigrison.' The use of ammonium chloride led to the production of hydrochloric acid in the mine gases, and it was consequently mixed with an equivalent quantity of sodium or potassium nitrate; or better, the alkali chlorides are themselves used (Bichel, Fr. Pat. 327868, 1902).

Modern German safety explosives contain large proportions of potassium or sodium chloride, and these explosives are very safe, especially in coal-dust mixtures, but are not so powerful as the older explosives.

The use of materials which absorb heat on decomposition, such as wood pulp and rye flour, has been found to confer great safety on explosive mixtures containing them, such as 'carbonite' and 'gelignite.'

The good effect of wood meal led to the manufacture of those safety black powders, like Argus powder and earthquake powder, containing a high percentage of volatile matter (*see* Curtis and others, Eng. Pat. 17878, 1898, and 6523, 1899). Some of the good effect of these slack-burnt charcoals has also been attributed to their reduced content of solid matter. Curtis and others (Eng. Pat. 6756, 1898) claimed the use of a layer of sodium bicarbonate in front of an ordinary gunpowder charge, the safety action depending on the liberation of carbon dioxide. The Westfälisch.-Anhalt. Sprengstoff. Actien-Gesells. (Eng. Pat. 3334, 1902) compound an explosive mixture so as to produce a large volume of ammonia on detonation; Reschke (Eng. Pat. 25780, 1905) suggests copper oxalate; von Dahman (Eng. Pat. 7562, 1898) suggests the use of acetic, citric, or tartaric acid and their salts with such explosives as roburite; Callenberg (Fr. Pat. 322946, 1902) proposes to add turpentine chloride; Macnab proposed to insert a glass tube containing aqueous ammonia into the gunpowder cartridge.

Testing Explosives.

The explosive characteristics of a powder depend primarily on its chemical nature. The analysis of explosives is consequently of great importance. As far as space would permit, an outline of the analysis has already been given under the individual explosives.

The purity of the ingredients, size of the grain, intimacy of the admixture and density, also largely influence the character of the explosive. A microscopic examination of a mechanical mixture, as with the cap composition, is of value.

An eye inspection of explosives that have been in store should be made for any sign of efflorescence and deliquescence or exudation, if a nitroglycerin explosive; and for signs of cracking or breaking down, in nitrocellulose powders; or local patches of discolouration in nitro powders generally. The development of acidity, as shown by the reddening of blue litmus paper, often indicates decomposition.

Stability Tests for Nitro Explosives.

One of the most desirable properties in explosives, whether for use as propellants or disruptives, is that they shall be chemically stable under all the conditions of climate, storage, and transport that they may have to withstand. All nitro explosives undergo decomposition at temperatures below, in some cases considerably below, their exploding-points, even when pure, and many of them are liable to contain traces of acids and impurities that are much less stable. The decomposition of these impurities leads to the production of higher oxides of nitrogen which act catalytically on the explosive itself, and may lead to the spontaneous ignition of the latter.

The extensive use of guncotton, dynamites, smokeless powders, and other nitro explosives necessitates the use of tests that will not only determine the stability of the ingredients themselves, but also detect the presence of any unstable impurities. The test should also be simple and reliable, and only take a short time to carry out. No single test has been devised that is universally applicable and will satisfy all these requirements, and it is usual to employ two, three, or more of the numerous tests that have been worked out and to form a definite conclusion on the combined results.

Unless otherwise mentioned, the tests apply only to nitrocellulose or nitrocellulose powders.

Deflagration test.—One of the earliest tests was that devised by Hess. The explosive was heated at a fixed high temperature, and the time of evolution of coloured fumes and also of firing was noted. In a modified test, the explosive was heated under pressure at 75° till explosion took place. This test, which is, at best, only a very rough indication of stability, is not much used at the present time, but is the basis of several other tests.

Fume test.—The test, devised by Thomas, consists in heating a definite weight of the explosive at a definite elevated temperature until brown fumes appear, the stability of the explosive being judged by the time taken. The method of carrying out the test with guncotton is as follows: 2·5 grams are weighed out into a well-cleaned glass tube 32 cm. × 1·6 c.m., and pressed down to a height of 4 c.m. The tube is closed by a well-fitting glass stopper and placed to a depth of 10 c.m. in an oil-bath, heated to 135°. At the end of 10 minutes, any moisture condensed on the upper part of the tube is wiped out. A standard tint for fixing the end of test is made by filling a tube with a solution containing 8 mgms. of potassium dichromate and 0·4 gram of cobalt sulphate per litre. The test is an official one in France and Holland, and is frequently used in combination with other tests; the temperature of the test being varied.

An objection to it is the length of time it takes for completion; for example, as used in Holland, guncotton heated for 10 hours a day at 95° requires 21 days before red fumes are developed.

Abel heat test is the English official heat test applied to nitro explosives generally, and is defined by the Explosives Act, 1875. The principle of the test is to note the time required to produce a standard discolouration of a test potassium iodide-starch paper, when the explosive is heated under specified conditions. The explosive is weighed out into test-tubes, about 5¼ to 5½ inches long, and holding 20 to 22 c.c. when filled to a height of 5 inches, which are closed by an indiarubber stopper, fitted with a

glass rod terminating in a platinum wire hook. On the hook is suspended a test paper, about 10×20 mm., the upper half of which is moistened with a mixture of equal parts of glycerol and water. The test papers, on the correct preparation and sensitiveness of which the test depends, are now made by the Home Office and by the War Office, and supplied to manufacturers of explosives. The test-tubes are placed to a depth of 3 inches below the cover, in a water-bath, the temperature of which is carefully regulated, at usually 160° or 180°F.. The water-bath is a spherical copper vessel, about 8 inches in diameter, fitted with a cover having a number, usually six, of circular holes, fitted on the under side with clips to take the tubes. The bath is fitted with a thermometer, the bulb dipping $2\frac{1}{2}$ inches into the bath, and usually some form of temperature regulator. The test is complete when the faint brown line which appears at the junction of the wet and dry parts of the test paper, which is adjusted to be $\frac{1}{8}$ inch above the cover, is equal in tint to the brown line on a standard-tint paper. This standard tint is a line drawn on paper of similar make to unprepared test papers, with a solution of caramel in water of defined strength.

The English Government specifications require that nitroglycerin displaced by water from dynamite, shall stand for 15 minutes at 160°F. (71°C.); blasting gelatin and gelatin dynamite 10 minutes at 160°F.; cordite and ballistite, 15 minutes at 180°F. (82°C.); guncotton and tonite, 10 minutes at 170°F. (76·6°C.); and gelatinised guncotton preparations for 15 minutes at 180°F. Smokeless powders are ground in a mill and sifted, and the portion retained between two sieves having holes equal to 14 and 21 B.W.G. respectively is used for the test.

In the United States, the first appearance of a brown line is taken as the end of the test, and the specified times are nitroglycerin, 15 minutes at 160°F.; blasting gelatin dynamite, 10 minutes at 160°F.; nitrocellulose for the Army 40 minutes, for the Navy 30 minutes, at 150°F. (65·5°C.); guncotton from compressed blocks, 10 minutes at 150°F.; nitrocellulose powders, 10 minutes at 100°F., and nitroglycerin-nitrocellulose powders, 20 minutes at 150°F.

In Germany, zinc iodide is used instead of potassium iodide in the preparation of the test papers, which are more sensitive than those prepared with potassium iodide.

This test is perhaps the most generally applicable and most frequently used. Objections that have been raised to it are that it is purely empirical, and depends largely on the conditions of its application, and further that it is really a test for traces of unstable impurities, and not of the absolute stability of the explosive itself.

Guttmann, in 1897, pointed out that the Abel test could be masked and falsified. With an explosive containing residual solvent, such as acetone, the test depends on decomposition of the nitro compounds, combined with the retarding influence of the solvent. In a similar way, the small quantities of stabilisers added to nitro explosives influence the time of test.

This is of little importance so long as these masking agents are recognised constituents of the explosive and present in their normal amount, or are extracted before the test is taken, as the limits of the test are fixed accordingly.

Mercuric chloride, which has a very strong masking influence on the heat test (as little as one part in 50,000 appreciably lengthens the heat test of cordite) is, in some countries, a recognised constituent of certain guncotton explosives, with the idea of sterilising them, but its use is not permitted in this country.

Modifications of the Abel test have been suggested, principally with a view of obviating the influence of masking agents. Guttmann (J. Soc. Chem. Ind. 1897, 287), for example, proposed a test paper treated with diphenylamine dissolved in sulphuric acid, which gives an intense blue colour with traces of nitrous acid; and Hoitsema (Zeitsch. angew. Chem. 1899, 705) proposed the same reagent used in a different manner. This indicator works well with guncotton explosives, but with nitroglycerin explosives the results are erratic, and they can also be readily masked.

Metaphenylenediamine was suggested as the best reagent by Spica, in 1899, but this again does not seem to work well with nitrocellulose-nitroglycerin explosives, and neither of the proposed modifications has been adopted.

Silvered-vessel test.—This test was devised at the Royal Gunpowder Factory, Waltham Abbey, to give an idea of the amount of deterioration that a sample of cordite had suffered, and from this to judge the further length of time it would be safe to store the cordite at any given temperature.

A silvered vacuum-jacketed flask is filled with the ground sample of cordite and exposed in a bath heated to a constant temperature of 80°. Readings of a thermometer, the bulb of which is in the centre of the cordite, are taken at intervals until the temperature rises 2° above that of the bath. The time taken for this rise of temperature of 2° is a measure of the stability of the cordite. The flask is fitted with a side tube in the neck, and the appearance of brown fumes in this tube indicates the active decomposition of the cordite, and serves as a warning that the test is near completion.

From the time of the test in hours, using a factor that has been established connecting rate of increase of deterioration of cordite with rise in temperature, the length of serviceable life of the cordite at any particular temperature can be calculated.

A newly made Mark I. cordite has a S.-V. test of from 500 to 600 hours.

German test.—In this test, which is largely used on the Continent and is one of the American Service tests, 2·5 grams of the air-dry explosive are heated in a glass tube loosely closed with a perforated cork at a fixed temperature, until a folded piece of litmus paper, fixed at 0·5 inch above the explosive, is completely reddened. The temperature of the test is 135°. The time limits are fixed by tests with standard samples of the particular explosive. Besides the time of complete reddening of the litmus, the time of the appearance of brown fumes and the time before the sample explodes, are also noted.

The American limits for this test are: for nitrocellulose and nitroglycerin powders, complete reddening over 30 minutes, brown fumes over 45 minutes, explosion over 5 hours; and

for colloided nitrocellulose, complete reddening over 75 minutes, brown fumes over 2 hours, and explosion over 5 hours.

Vieille test.—This test is the French Service test. 10 grams of the explosive are weighed out, and a piece of standard blue litmus paper is also introduced into a glass tube which is closed as tightly as possible by means of a clamped well-fitting stopper. The tube is heated in a bath maintained at 110°. When the litmus paper is completely reddened, the time is noted and the tube cooled. The sample with a fresh piece of litmus paper is introduced into a second tube and the heating continued. This process is repeated until a period of less than an hour is taken to completely redden the litmus paper. The sum of the number of hours of the previous heatings is then taken as the time of the test.

Vieille found that, as the temperature of the test was raised, the time is reduced in arithmetical progression, and concluded that 110° is the best temperature for giving reliable results within a reasonable time.

'Poudre B.' has a Vieille test of approximately 50 hours.

There is a gradual loss of nitrogen from the powder during the test which Vieille found to be approximately 0·009 p.c. nitrogen per hour, during a test of 100 hours (Mém. des Poudres et Salpêtres, 1909, 71). The decrease in the nitrogen content, and the time taken to first redden the test paper, are both considered in conjunction with the total time of the test in sentencing a powder.

Will test.—This test gives a quantitative idea of the stability of a nitrocellulose, and is very largely used in conjunction with such tests as the Abel test. The test, which is fully described by Will in the Mitt. aus der Centralstelle f. Wissensch. Tech. Untersuchungen, 1900, [2] 5, and 1902, [3] 34, is based on the measurement of the nitrogen evolved from guncotton when heated at a temperature of 135°. 2½ grams of the dry nitrocellulose, or 3½ grams of moist nitrocellulose as it leaves the centrifugal machines, are weighed out into a glass decomposition tube and compressed to a given volume. This tube is connected at one end with a preheating glass coil, and is fitted at the other end with a well ground-in exit tube. The tube is placed in an oil-bath fitted with a stirrer, the temperature of which is carefully regulated to 135°. To remove the products of decomposition as fast as they are formed, a uniform current of purified, air-free, carbon dioxide is passed over the heated nitrocellulose at a rate of about 25 c.c. per minute. The gases after passing over heated copper gauze, contained in a heated copper U-tube, to reduce the oxides of nitrogen, are collected over caustic potash in a gas burette, with a special zigzag arrangement to give thorough absorption of the carbon dioxide. The column of the nitrogen collected is read off first after 30 minutes, then after every 15 minutes for a period of about 4 hours, the caustic soda being frequently renewed. Explosions may occur, and the oil-bath is surrounded by a strong screen. The results are plotted on a curve. The gas from a stable nitrocellulose should be evolved at a uniform rate, and, if this is so, Will considers that the sample is normal, or has attained a 'limit state' of purification. With unstable samples, the gas evolution is much greater at first than later in the test.

To interpret the results given by any nitrocellulose explosive, a set of standard curves must be obtained from well-purified samples for purposes of comparison. English Service guncottons average an evolution of 7·5 mgms. ± 1 mgm. of nitrogen per 4 hours (Robertson).

Reiss test.—This is a modification of the Will test, in which the decomposition is effected at 135° *in vacuó*.

This modification is the one usually applied to high explosives of the nitro class, the temperature of the bath and time of heating varying with the explosive. The decomposition tube is connected by means of a well-fitting stopper, having a mercury lute with a long mercury manometer tube in which the gas volumes are read off at intervals for some days, and the results, corrected to N.P.T., plotted and interpreted by reference to curves obtained from standard samples.

Obermüller test.—This test is similar to the last, except that the gas volumes are not calculated, but the pressures exerted by the evolved gas, the volume of which is kept constant, are recorded. The rate at which the pressure increases is taken as a measure of the decomposition, and so of the instability of the explosive. For nitrocellulose, the temperature of the test is 140°. Mittasch (Zeitsch. angew. Chem. 1903, 929) describes a similar test in which the gas evolution is automatically recorded.

Bergmann and Junk test.—This test gives very reliable results, and has been largely used, especially in Germany. 2 grams of the dry nitrocellulose are weighed out into a tube 35 cm. long and 2 cm. wide, and pressed down. The decomposition tube is connected with a ground-glass stopper connected with an absorption bulb containing water. The explosive is heated for 2 hours in a bath, kept at a constant temperature of 132° by boiling amyl alcohol. The decomposition tube is then allowed to cool, and the water to flow back on the explosive. The contents of the tube and apparatus are washed and filtered, the filtrate oxidised with permanganate, and the nitrogen estimated as nitric oxide by the Schulze-Tiemann method. The limits of gas evolution fixed are 2·5 c.c. of NO per gram guncotton, or 2 c.c. per gram collodion cotton. This test is considerably influenced by the amount of moisture present in the sample.

Sy test.—This is a U.S. Service test (J. Amer. Chem. Soc. 1905, 549). 1 to 4 grams of the explosive are weighed out on a covered watch glass and heated in an air-bath, maintained at a constant temperature of 115° by a boiling mixture of xylene and toluene. After 8 hours' heating, the watch glass is cooled and weighed, and the process repeated daily for some six days or more. The daily loss in weight, mgms. per 1-gram sample, is plotted out, and comparison made with standard curves. The advantages claimed for this test are that whole pieces of the powder are tested, and that all volatile products of decomposition are determined.

Jacqué test is a modification of the above, made in order to reduce the time of the test (Zeitsch. Ges. Schiess- u. Sprengstoffwesen, 1906,

395). The sample is heated at 130°–140°, and weighed after successive 2 hours' heating.

Intensity of Action of Explosives.

The intensity of action of an explosive depends on the volume of gases produced, on their temperature, and on the velocity of explosion or detonation of the substance.

Closed-vessel experiments.—The volume of permanent gases and the quantity of heat evolved have been determined for many of the more important explosives; but the gases collected and examined are those remaining after cooling down to atmospheric temperatures, not those existing at the period of maximum temperature. The uncertainty as to the nature and the specific heat of the products of explosion at the high temperatures produced, renders the calculation of quantity of heat into temperature hazardous. The experiments are carried out with different densities of charge in some form of steel bomb, similar to Berthelot's calorimetric bomb, as used in the experiments of Abel, Noble, Deering, Macnab, and others already mentioned, details of which are given in the papers referred to.

The pressures developed in the bomb are usually measured by a *crusher gauge*. This consists of a small steel cylinder, closed at one end, into which a collar screws gas-tight. A piston working through the collar fits against a small cylinder of copper resting on the bottom of the cylinder chamber. On firing the explosive, the gas pressure acting on the end of the piston compresses and shortens the copper cylinder. The pressure in tons per square inch corresponding to the reduction in length of the cylinder, accurately measured on a micrometer scale, is obtained from tables compiled from the compressions produced by various statical pressures. Other methods of measuring the pressure are used. Deering checked the results obtained with the crusher gauge by closing an orifice of the bomb with a steel ball held in position by heavy lead cylinders. The weight was gradually reduced until the pressure was sufficient to lift the load. Several pressure gauges have been invented for directly measuring the pressure. For example, Bichel (Eng. Pat. 18273, 1898) has designed a gauge, fitted into the explosion vessel, which records the pressure developed by means of a pencil working on a drum, rotating by clockwork. Some knowledge of the rapidity of the explosive is also obtained by the steepness of the curve recorded, and the pressure of the cooled gases is indicated when the curve becomes horizontal. From the latter and the volume of the chamber, the volume of permanent gases can be calculated. Petavel (Proc. Roy. Soc. 1905, 492) describes a method of measuring the pressure developed by explosives by means of a specially constructed manometer which records photographically on a revolving cylinder.

The attempts of Macnab and Ristori to experimentally measure the temperature of explosion have been already referred to. Bichel has attempted to obtain an idea of the temperature of explosion by taking spectrum photographs of the flames produced on detonation.

Information of value, concerning the intensity of action of explosives, may be obtained by detonating a charge (a pound or so in weight) buried in earth, and observing the size of the crater; or by noting the reaction effects (the dimensions of the crater) produced on undisturbed earth, or the bulge or hole produced in wrought-iron plates, by the detonation on them of the explosive; comparison being made with an equal weight of guncotton or other known explosive, the charges having the same area and shape (most conveniently cylindrical).

Lead cylinder method: Trauzl test.—In this method the enlargement of the cavity in a lead block of given dimensions gives a measure of the power of the explosive. Abel's results, quoted in this article, were obtained by this method, using cylinders of soft, pure lead, 12 inches high and 12 inches in diameter, with a central cylindrical hole 7 inches deep and 1·3 inch in diameter, in which 1 oz. of explosive is detonated. With cylinders of these dimensions, no cracking through of the bottom is to be anticipated; the diameter of the bore hole just takes a service 1 oz. dry guncotton primer, which is used as a standard of reference. The lead cylinder is placed on a stout iron plate, the weighed explosive (cast or compressed into a cake, or rammed to a known volume in the bore hole, according to circumstances) with a mercury fulminate detonator (or suitable priming such as will produce a maximum effect on detonation) inserted into it is placed at the bottom of the bore hole, the latter filled with fine sand poured into it without pressure, and the detonator fired electrically or by safety fuse. The volume of the cavity produced is ascertained by means of water and a graduated vessel, and the volume of the bore hole being deducted gives the enlargement. With an unknown explosive, several experiments are necessary to ascertain the best conditions of detonation. This test is only reliable for the comparison of explosives of the same type, and the results obtained with slow-acting explosives are of little value. The higher the velocity of detonation, the greater the expansive effect.

Standard conditions for carrying out this test were suggested by the 5th Inter. Congress of Applied Chemistry, Berlin, 1903. The standard dimensions of the lead cylinder are, height 200 mm., diameter 200 mm., with an axial bore hole 125 mm. deep and 25 mm. diameter. The lead must be pure and soft and the cylinders used in a series of tests must be cast from the same melt. The temperature of the cylinder must be uniform throughout and between 15° and 20°. 10 grams of the explosive are formed into a cartridge 25 mm. in diameter by wrapping in tinfoil, weighing 80–100 grams per square metre. An electric detonator with a charge of 2 grams is placed in the midst of the explosive. The charge is gently pressed to the bottom of the bore hole by means of a wooden stick and the bore hole filled up with dry quartz sand. After firing, the cavity is brushed out and finally measured.

Abbot's ring apparatus.—Many of the earlier values for the intensity of action of explosives were obtained by Abbot in the ring apparatus described in his classical report upon 'experiments and investigations to develop a system of submarine mines' (Washington, 1881). The explosive was contained in a suitable case fixed

in the centre of a wrought-iron ring 4 feet in diameter into which six lead crusher gauges were fixed at equal intervals. The apparatus was submerged in deep water, and the explosive fired electrically. The explosive force was obtained as usual from the shortening of the lead cylinders.

McRoberts has described a method of comparing explosives by the reaction effect their detonation produces on a pendulum-hung mortar weighing about 600 lbs. The distance from the centre of suspension to centre of trunnions is exactly 10 feet; the mortar is set with its axis horizontal. 10 grams of explosive are placed in a small recess behind the chamber for the projectile; the latter weighs about 40 lbs. and fits the bore gas-tight. The explosive is fired by means of a fuse and detonator; the angle of recoil of the mortar is marked on a graduated index by a pencil which the former carries. The work done by the explosive is twice that done in raising the mortar through the versed sine of the angle of recoil; this is expressed in foot-pounds.

Velocity of detonation. The old method of determining the rate of detonation was to place a number of cartridges end to end, pressed well in contact with one another, so as to form a continuous length of the explosive. This cord of explosive was fired at one end by some efficient detonating agent, and the time of explosion was taken by a Boulengé electro-ballistic chronograph, as described under 'Ballistics of a propellant,' the two electric currents being successively interrupted by the firing of the two ends of the cord.

The results of numerous experimenters showed that the velocity of detonation increased, up to a certain point, with the diameter of the train of explosive. These experiments required a large bulk of explosive, the train of explosive being usually about 3 cms. in diameter and 35 metres in length, so that they were both costly and dangerous to carry out.

Mettegang's recorder.—An improved, purely electrical method of determining the velocity of detonation was described by Mettegang, at the 5th Inter. Congress of Applied Chemistry, Berlin, 1903. It is a modification of Siemens' apparatus for measuring small intervals of time. The method depends on the consecutive interruption of two wires, carrying a divided current, running through two ends of a long cartridge and connected with a sparking induction coil. The main current passes through a resistance of electric lamps, and to ensure a high potential, no iron core is used in the primary. Any change in the tension of the current passing through the primary coil sets up an induced current in the secondary coil. One terminal of the secondary coil is connected to the bearing of a revolving drum coated with lampblack, the other terminal ending in a fine platinum point. The induced currents cause sparks from the platinum point which are recorded as tiny specks on the blackened surface of the drum. From the space between these specks and the speed of the drum, the time of detonation of the explosion train is found. The cartridges of the explosive are 3 cms. in diameter, and a total length of 3 to 4 metres is used, the cartridges being enclosed in an iron pipe and buried in sand.

The highest rate of detonation recorded in experiments with numerous explosives is about 8000 metres per second. A 4-metre length of explosive would therefore detonate in $\frac{1}{2000}$ of a second, and with a rotary speed of 25 metres per second the markings on the drum would be 12·5 mm. apart.

The velocity of detonation of explosives has been determined by Dautriche (Compt. rend. 1906, 143, 641), by a method depending on the use of detonating filaments, which had a constant and determined velocity of detonation of 6500 metres per sec.

Two equal lengths of the filament are detonated, one of which is cut, and a tube filled with the explosive is interposed. One end of each filament is fixed to a detonating charge of fulminate, the other ends are bound together and fixed on a lead plate. The retardation of the velocity of detonation of the filament with the length of explosive introduced, causes the displacement of a depression mark on a sheet of lead from the position given when two equal uncut filaments are used. This displacement with the known velocity of detonation of the filaments give the time of detonation of the given length of the explosive.

Character and duration of flame. The photographing of the flame of explosives was first attempted by Schoeneweg, the inventor of securite, and is now very largely used in determining the character of the flames of mining explosives, propellants, and cap compositions.

In testing the flame of explosives, they are fired at night from a vertical steel cannon with a graduated scale placed behind it. The flame is photographed upon a drum covered with a sensitised film, rotating between screw pivots in a guide bracket, contained inside a box provided with a quartz camera lens for focussing the ultra-violet rays attending extreme heat. With the drum at rest, the length of the flame is obtained. To obtain the duration of the flame, the drum, which is motor-driven, is set in motion, and as soon as the required speed is obtained, the shot is fired electrically. From the speed of the drum and the lateral extension of the blurred image of the flame, the duration of the flame is obtained. According to Bichel, the limit values for the length of flame of a safety explosive lie between 0·4 and 2·24 metres, and the limit values for the duration of flame between $\frac{0{\cdot}28}{1000}$ and $\frac{10}{1000}$ of a second. Coal carbonite and blasting gelatin were taken as representing the two extremes.

Bichel compares the '*after-flame ratio*' of different explosives, that is, the ratio of the velocity of detonation, taken as unity, to the duration of the flame, as an indication of their safety. This ratio for coal carbonite is 1 : 8·7, and for blasting gelatin 1 : 883, so that Bichel concludes that the former is 100 times as safe as the latter. The flame of all explosives outlasts the time of detonation, but that of the safer explosives does so in much less degree than those of the less safe.

Ballistics of a propellant. So far as explosives are concerned, only the internal ballistics are meant when ballistics are referred to, that is, the phenomena which takes place from the time ignition is brought about until the projectile is

clear of the influence of the explosion gases. The ballistics concern principally the pressures developed in the gun and the muzzle velocity of the projectile. They can be calculated with some degree of accuracy for any particular gun, with any special nature and form of propellant, knowing the gravimetric density of loading, that is, the ratio of the volume of the powder to the capacity of the gun chamber, and the chemical composition and rate of burning of the powder. When explosion first takes place, the gun chamber may be looked upon as a closed vessel, so that the intensity of the initial chamber pressure and the rapidity with which it develops, depend directly on the loading density. The pressures obtained in a closed vessel are, however, never attained, owing to the motion of the projectile enlarging the chamber and lowering the gravimetric density.

In practice, the *pressures* attained in the bore of a gun are measured experimentally by means of crusher gauges, which are screwed into the bore of the gun at regular intervals, but in the ordinary proof testing of a propellant only the maximum chamber pressures are determined by means of a crusher gauge placed in the chamber. These crusher gauges have already been described in connection with the measurement of closed-vessel pressures.

In proving propellants, the *velocity* that a given charge will impart to a projectile in a particular gun, is determined by means of a Boulengé chronograph or some modification of this apparatus. The time taken by the projectile to pass over a known distance is determined in terms of the space passed through by a freely falling body in the same time. The projectile cuts through wires stretched on two frames a known distance apart. The cutting of the wire on the first frame liberates a rod suspended by an electro-magnet. The cutting of the wire on the second frame puts into action, by means of a second dropping rod falling through a shorter distance, a knife edge, which makes a nick in the first falling rod. From the space fallen through by the marked rod, the time for the projectile to pass over the distance between the two screens can be calculated.

In testing the ballistics of nitro propellants, they are heated to a definite temperature for some time before firing.

Bibliography.—A chronological bibliography on explosives up to the year 1895 will be found in the second volume of Guttmann's The Manufacture of Explosives.

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EXTRACTION APPARATUS. The object of extraction is to dissolve out some constituent or constituents from a substance by treating it with a solvent. When the substance is a solid, it may be allowed to soak in the solvent at ordinary temperatures (*maceration*) or at higher temperatures (*digestion*), the solution being after a time poured off, both methods being included under the term *infusion*; a third method is to boil the substance with the solvent (*decoction*); and a fourth is to allow the solvent to descend through a column of the substance placed in a suitable vessel (*percolation* or *displacement*).

The treatment when the substance is a liquid will be considered further on.

Processes of extraction are involved in many of the large industries; for instance, in brewing; in the 'diffusion' process of obtaining sugar from sugar beet or sugar cane; in the 'lixiviation' employed in the manufacture of various inorganic salts, &c., &c.; and descriptions of them will be found elsewhere. Besides these, extraction apparatuses are employed in the laboratory of a small size for quantitative work, and on a larger scale for making various preparations; in the manufactory they are used for preparing medicinal extracts, alkaloids, dyestuffs, tanning materials, and volatile oils, and in removing oil from seeds and fat from bones.

An account of some of the numerous forms employed is given below.

When water is the solvent employed, the operation may be conducted in a large copper pan fixed in an outer jacket of iron, so that a space is left between the copper and the iron through which steam can be made to circulate and heat the contents of the pan. Such pans are either fixed and have a pipe and tap at the bottom to draw off the solution, as shown in section (Fig. 1) or else they are movable about

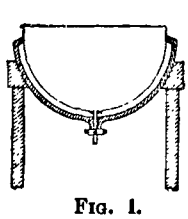


FIG. 1.

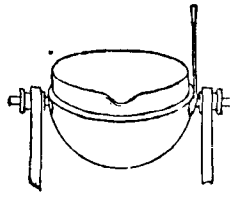


FIG. 2.

an axis (Fig. 2), so that the pan can be tilted and the solution poured off; in these, the axes on which the pan rotates are tubular to permit steam to enter and escape from the space between the pan and its iron jacket. When the infusion has been continued for a suitable time, and the liquid has been drained off, the residue is placed in a canvas bag and subjected to strong pressure in a screw press, in order to squeeze out as far as possible the last portions of the solution. A common form of press consists of a base to which two uprights with a cross bar at

top are fixed; in a thread cut through the centre of the cross bar works a powerful vertical screw. Between the uprights is a strong metal or wooden cylinder perforated with a number of holes; in this the bag of residue is placed, and on top is placed a thick plate which transfers the pressure exerted by the screw to the bag and its contents. The cylinder rests in a tray of a somewhat wider diameter, and provided with a spout: this tray collects and conducts off the expressed liquid to a vessel placed beneath the spout. Instead of pressing the residue, it may be infused several times more with water until it is completely exhausted of the desired constituents, but this method involves a large amount of subsequent evaporation. The solutions obtained by the above processes are next strained through conical bags of linen or flannel, and then evaporated down in jacketed pans like those previously described, the liquid being kept in motion by a mechanical stirrer.

In many cases, evaporation at temperatures near 100° has an injurious effect on the substances in solution, and some arrangement for evaporation in a partial vacuum is adopted; this enables the evaporation to be conducted at a lower temperature than when the liquid is subjected to the pressure of the atmosphere.

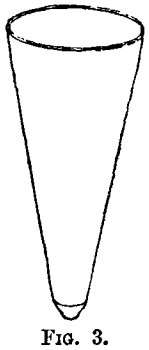


Fig. 3.

In the process of *percolation* or *displacement*, the powdered substance is placed in a long cylindrical or conical vessel (Fig. 3), and rests on a perforated disc placed near the bottom and which can be covered with a piece of linen or flannel. A conical vessel is preferable to a cylindrical one, as the mass adjusts itself more readily to the vessel when any change of volume occurs; in a cylinder, if the mass swells on absorbing the solvent, it is apt to become so tightly packed that the liquid cannot pass, or, if it contracts owing to the removal of soluble constituents, it is more liable to form cracks and channels. A second perforated disc of linen or of paper pierced with holes is laid on top of the substance to distribute the solvent uniformly. It is often advisable to damp the powder with about half its volume of the solvent before packing it into the percolator, otherwise some portions may be found to have escaped getting wet during the whole operation. Care must be taken in packing that the substance is throughout in as uniform state of compression as possible, or else the solvent will pass more freely through the loosely packed portions. Different substances require to be packed with different degrees of tightness; and when alcohol or ether are the solvents employed, the packing may be tighter than in the case of water, as they do not cause such a swelling of the substance as water does. The conical vessel is supported in a circular hole cut in a table or wooden stand, a vessel is placed underneath to receive the solution, and the solvent is poured from time to time on the top. A row of such percolators can be arranged so that the solution from the first is poured on to the next and so on along the row, by which plan the liquid from the last will be a strong solution, and the percolators that are more nearly exhausted will receive the weaker and therefore more active liquids.

For some purposes, more elaborate forms of aqueous extraction apparatus are preferable. Of these the following is an example:—

Hänig and Reinhard's apparatus (Fig. 4).—This is designed for extracting dyewoods, &c., by the action of steam and water. A and B are two similar vessels (A is shown in section) which can be made to revolve about the axes *xy*, *xy*, by means of the gearing G, G, so as to facilitate filling and emptying. The axes are tubular and serve for conducting steam and water. In communication with the axis *x* are two pipes having taps *a'* and *a*; one ascends and leads into the upper part of the vessel, and the other descends, and, passing through the bottom of the vessel, leads to a perforated pipe, *g*, which forms a ring underneath a perforated false bottom, *h*. Communicating with the axis *y* is a pipe which descends and, following the dotted lines, joins on to the back of the three-way tap *b*. This tap *b* communicates with the space beneath the false bottom and also with the air. Another three-way tap, *c*, affords means of communication between the two axes *y*, *y*, and also with a pipe at the back indicated by the circle of dots. The covers of A and B can readily be taken off and fastened on again by the row of screws *s*, *s*, *s*. These covers form the condensing apparatus; inside they possess one or more flat horizontal coils *w*, *w*, to which water enters through the tube *m*, and escapes through *n*, and then flows over the whole lid, forming a layer on the top, and is thence conducted away. *e* and *f* are openings for air and safety valves, and *d*, *d*, *d* are taps for ascertaining the level of the liquid inside the vessel.

To work the apparatus A and B are filled with the substance to be extracted, and the covers are fastened on. A suitable quantity of hot water is introduced into A through the tap *c*, placed in such a position that it passes down the pipe *t* and through the tap *b* into A. Steam is now passed in through the axis *x*, and through the valve corresponding to *a*, and escapes through the perforations of the pipe *g*, heating the water and the substance and ascending to the top, where it is condensed and flows as liquid back to the bottom again. The action is further accelerated by opening the valve corresponding to *a'*, and passing steam in at the top of the apparatus. The first few solutions, which are strong, are drawn off by the tap *b*, then the later and weaker ones are forced by the pressure of the steam into the vessel B, the taps *b* and *c* being placed so as to lead to that vessel. A is then emptied and refilled with fresh material, and B is now worked in the same way that A was. By proceeding in this way alternately with A and B, the later and weaker solutions from one vessel come into contact with fresh material in the other and become strong, and thus economy in evaporation is effected (Ger. Pat. 18922, 1881; and Dingl. poly. J. 1882, 246, 22, a later form of that in Ger. Pat. 10771, 1880, and Dingl. poly. J. 1880, 238, 332).

Solvents other than Water.

When solvents other than water are used, it becomes desirable to avoid the loss that would

be involved in pouring off the solvent and pressing the residue, and also to make a minimum of solvent do a maximum of dissolving; numerous forms of apparatus have been devised to attain these ends, the principle involved being to distil off the solvent from the solution and use it over and over again, and many of the forms are arranged so as to work continuously and to require but little attention. There are three main plans on which they are constructed. In one, continuous percolation is effected; in the second, continuous infusion, an overflow tube conducting the solution from the bottom of the column of substance and allowing it to escape at a level slightly above the top of the column; and in the third, intermittent infusion is the result attained. This last plan has the advantage of removing one lot of solution and bringing quite fresh solvent into contact with the substance from time to time; since 1879 it has been brought to a high degree of perfection by exchanging the overflow tube of the second plan for a siphon, which makes the action an automatic one. Below are given descriptions of well-known or typical apparatuses, and also references to other forms that have been described. Apparatuses suitable for the laboratory are taken first, and are grouped on the

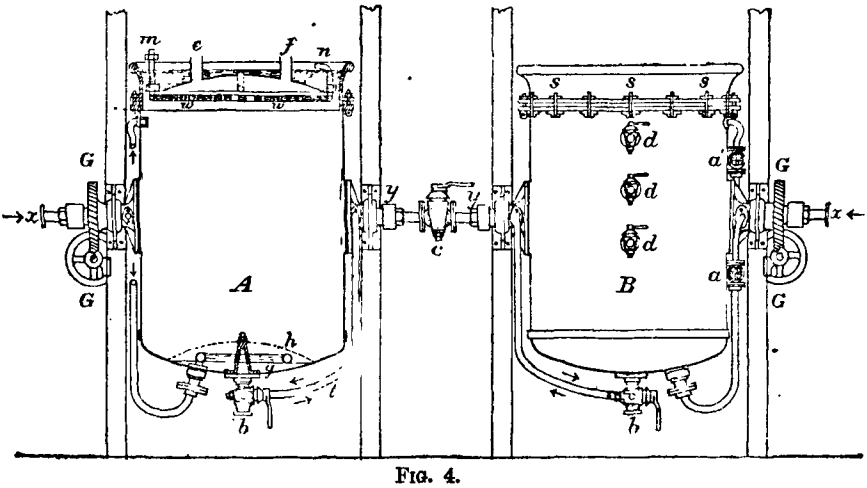


FIG. 4.

classification given above, percolation forms coming first and the two infusion groups next. Then follow some examples of manufacturing plant.

Laboratory Forms.

Mohr's apparatus (Fig. 5).—This is an early form, often referred to in older chemical literature.

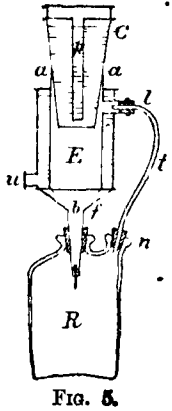


FIG. 5.

The substance to be extracted is placed in the cylinder E, and rests on a piece of fabric placed on a perforated curved plate *b*, which forms the bottom of the inner cylinder. The solvent is then poured on to it, and the top vessel C is put in its place; it fits into the top of the inner cylinder, making an air-tight joint at *a*. A funnel, *f*, which forms the lower external part of the middle piece of the apparatus, fits into the centre neck of a Woulff's bottle, R, and conducts the solution into the bottle. The solvent is evaporated off by placing the bottle in a vessel of hot water, and its vapour passes by the tube *t* back into the inner cylinder E, and is there condensed and brought into use again by causing cold water to circulate in the space between the inner cylinder and the outer wall of the apparatus; the water is run into this space through the tubulure *u*, and escapes by an overflow pipe not shown in the diagram. The top vessel C also forms part of the condensing apparatus; water is run into the top of it, and passes down the centre pipe *p*, then rises and fills the vessel C, and is conducted away by an overflow pipe. The two upper pieces of the apparatus, E and C, are constructed of metal.

When the extraction is complete, which can be seen by the solvent dropping colourless from the funnel, the excess of solvent is recovered by removing the tube *t*, corking the neck *n* of the Woulff's bottle, and connecting the tubulure *l* with a Liebig's condenser. The vessel C is emptied, as also is the annular space of the middle cylinder, and the cold water in the latter is replaced by hot. This causes the solvent that the substance has absorbed to distil off, and it can then be collected at the end of the Liebig's condenser. The top vessels are next removed, and by connecting the Woulff's bottle with the Liebig's condenser, the rest of the solvent can be obtained (Mohr's Lehrbuch der Pharm. Technik, 1847, 108).

Jacobi (Dingl. poly. J. 1862, 164, 343) has described some improvements in Mohr's apparatus.

Hoffmann's apparatus (Fig. 6).—The substance to be extracted is mixed with fragments of glass and placed in the short wide tube E, which is closed at the bottom with a plug of cotton wool. The solvent is placed in the weighed flask R, and then converted into vapour by placing the flask on a water-bath; the

vapours pass up past the substance and through the tube T into a second flask, C, kept cool by being immersed in water or in a freezing mixture, and are there condensed. The air escapes by

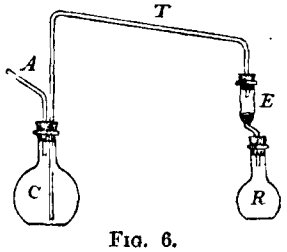


FIG. 6.

the short elbow tube A. When all the solvent has been boiled off from R, the water-bath is removed, and as R cools the pressure of the atmosphere forces the solvent back through T and E into R, dissolving and washing out on its way the soluble constituents of the substance undergoing extraction. The solvent is again boiled off from R, leaving the soluble matter behind, and the operation is repeated several times until the substance ceases to yield anything to the solvent. The solvent is then evaporated off for the last time from R, which is at once disconnected, and heated in a water-bath until it ceases to lose weight (Zeitsch. anal. Chem. 1867, 6, 370).

Von Bibra's apparatus (v. Gorup-Besanez's Anleitung zur zoo-chem. Analyse, 1850, 353) differs very slightly from that of Hoffmann.

Storch's apparatus (Fig. 7).—In a wide and somewhat conical glass tube E (the neck of a retort will answer), there is placed a tube, *t*, with its lower end projecting a little below the narrow end of E, where a plug of cotton wool, fairly tightly packed, serves both to keep the tube *t* in its place and also to form a support for the substance to be extracted. The substance is filled into E up to within half an inch of the top of *t*, which is temporarily plugged with cotton wool during the filling operation, in order to prevent any of the substance entering it. The

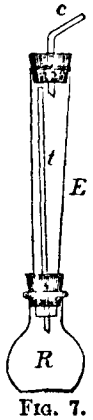


FIG. 7.

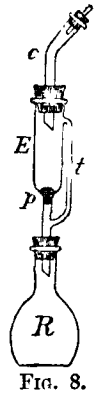


FIG. 8.

extractor E is fixed by a cork into a flask R containing the solvent, and its top is closed by another cork, through which passes a tube *c* leading to a condenser. On warming R on a water-bath, the vapours of the solvent ascend through *t*, escape by *c*, and, when condensed, flow back and percolate through the substance undergoing extraction. The cross section of *t*, without being too small, should be less in area than that of the space between it and the outer tube E at its lower end; otherwise, the downflow of the solution is impeded. This apparatus is designed for quantitative analyses, but it can also be constructed of metal and used for larger operations (Zeitsch. anal. Chem. 1868, 7, 68).

Vohl (Dingl. poly. J. 1871, 200, 236) has described an apparatus on a plan similar to Storch's, but it is more elaborate in its fittings.

Gantter's apparatus (Dingl. poly. J. 1880, 236, 221) is on a plan similar to that of Storch.

Zulkowski's apparatus (Fig. 8).—This is a modification of that of Storch. The substance is placed in the extractor E, and is supported by a plug of cotton wool, *p*. The vapours of the solvent, as they boil off from the flask R, pass upwards through the side tube *t*, which is fused

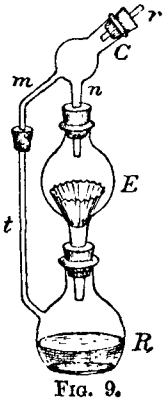


FIG. 9.

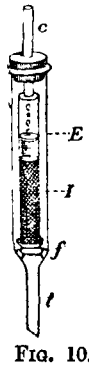


FIG. 10.

on to E, and then pass through the adaptor *c* to a condenser. The condensed liquid flows back and percolates through the substance in E, and drops again into R (Zeitsch. anal. Chem. 1873, 12, 303).

Maly (Annalen, 1875, 175, 80), Wolfbauer (Ber. der Versuchsstationen, Wien, 1878, 1), Weigelt (Repertorium der analytischen Chemie, 1881, 1, 7), and Flückiger (Zeitsch. anal. Chem. 1882, 21, 467) have described apparatuses which resemble or else are modifications of that of Zulkowski.

Drechsel's apparatus (Fig. 9).—A folded filter, having double the usual number of folds, so that it may fit well to the sides of the vessel, is placed in the glass globe E, and on this paper the substance to be extracted is put. The solvent is placed in the flask R, which has a tube *t* fused into its side; on warming R the vapour ascending through *t* and through the tube *m*, which is held in contact with *t* by a cork and is fused on to the glass apparatus C, passes on to a reflux condenser connected with C by the tube *r*. The condensed liquid flows back into C, and is led by the tube *n* into the globe E where it falls on the substance, and after having percolated through it returns to R again (J. pr. Chem. 1877, 123, 350).

Payen's apparatus is somewhat similar to that of Drechsel. In the place of E, there is a

long conical vessel in which the substance rests on a cotton wool plug, and the tube *t* proceeds from a tubulure and cork in B, and bends over at the top and passes through the cork at the top of E (Ann. Chim. Phys. 1845, [3] 13, 59).

Kopp's apparatus (Comptes rendus des Travaux de Chimie par Laurent et Gerhardt, 1849, 5, 305) is an improved form of that of Payen.

Weyl's apparatus (Zeitschrift für Instrumentenkunde, 1885, 5, 126) is an arrangement like Drechsel's, but by the employment of mercury joints an ordinary funnel can be used instead of the glass globe E.

Gwiggner's apparatus (Zeitsch. angew. Chem. 1902, 15, 882) consists of a vessel in which a funnel with the filter paper in position can be placed and the substance on the filter extracted by a volatile solvent. The vapour of the solvent rises between the funnel and the outer vessel, and when condensed drops from a ring of points on to the edge of the filter paper. It is useful for extracting sulphur from precipitates and in other analytical operations.

Tollens' apparatus (Fig. 10).—This is an improvement on an earlier form which was described by Tollens (Zeitsch. anal. Chem. 1875, 14, 82). The substance is placed in the inner tube I, which is slightly contracted at the bottom *f*, and then spread out into a rim over which a piece of filter paper is tied. This tube I is placed in a wider tube E, and rests on a bit of bent glass rod at *f*, which prevents it from closing the aperture into the narrower part *t*. The neck *t* is fitted by means of a cork into a flask containing the solvent, the vapours of which ascend through the space between I and E, and then through *c* to the condenser. The condensed liquid drops into I, and after percolating through the substance passes through the filter paper and back into the flask again (Zeitsch. anal. Chem. 1878, 17, 320).

FIG. 11.

A form, having an extraction tube with a pointed lower extremity, is described by Dunstan and Short (Pharm. J. 1883, 13, 663).

Schulze and von Rampach's apparatus (Fig. 11).—This was an improvement on the earlier form of Tollens' apparatus. It resembles Tollens' later form, with the exception that the inner tube I in which the substance is placed passes through and is held in its place by the cork at the top of the outer tube E. The inner tube I is connected with a condenser, and is perforated just below the cork with one or more holes through which the ascending vapours pass and enter the condenser (Zeitsch. anal. Chem. 1878, 17, 171).

Scheibler's 1st apparatus (Ger. Pat. 3573, 1878, and 7453, 1879; Dingl. poly. J. 1879, 234, 128), and also those of West-Knights (The Analyst, 1883, 8, 65) and of Bensemann (Repertorium der analytischen Chemie, 1886, 6, 390) differ but little from Schulze and von Rampach's.

Gawalowski (Zeitsch. anal. Chem. 1883, 20, 528) describes some improvements in percolating forms of extractors; one of these is to provide a stop-cock to close at will the side tube up which the vapours ascend; if this is closed from time to time and the source of heat is removed, the contraction in the flask sucks the liquid through the substance undergoing extraction. Another is to employ an arrangement like Drechsel's in addition to and underneath an improved form of Zulkowski's tube, whereby perfect filtration is attained.

One disadvantage in the percolation apparatus is that the drops from the condenser always fall on nearly the same spot of the surface of the substance, so that some portions do not get such a good chance of being extracted as others. To remedy this, Barbier (J. Pharm. Chim. 1878, [4] 27, 200) employed an apparatus in which a siphon in a vessel above the percolator pours a considerable volume of the solvent from time to time on the substance, so that the surface of the latter becomes covered with a layer of liquid. The apparatus of Guérin (J. Pharm. Chim. 1879, [4] 30, 511), Stockbridge (Chem. Zentr. 1885, [3] 16, 280), and of Wollny are others that adopt this plan, and that of the last-mentioned is given below as a type of the class.

Wollny's apparatus (Fig. 12).—This consists of a receiving flask R to contain the solvent, and two other pieces shown in section in the figure. These bits are united together by the mercury joints *a*, *b*, *c*, *d*, which are provided with small tubes to permit of their being emptied without tilting the apparatus. The top joint *d* connects the apparatus with the condenser. The substance to be extracted, contained in a cartridge of paper which must be permeable by the vapours, is placed in the tube E. The vapours of the solvent ascend the tube *p*, and then pass downwards through E, heating the substance on their way, into the space F, whence they escape up the tube *t* to the condenser. The condensed liquid collects in the vessel V, and is siphoned off from time to time by the tube *s*, thus ensuring the complete extraction of the substance. The solution returns through F and the long tube *q* to the flask again. In cases where boiling the solution injures the dissolved constituents, vapours of the solvent can be introduced through the side tube *r* from another vessel of solvent heated separately, and the flask R can be left cold (Zeitsch. anal. Chem. 1885, 24, 48).

References to other authors who have described forms of percolation apparatus are: Robiquet (J. Pharm. Chim. 1851, [3] 20, 168); Dragendorff (Zeitsch. anal. Chem. 1862, 1, 490); Berjot (Bulletin de la Société d'Encouragement, 1862, 61, 396) and Wagner (Zeitsch. anal. Chem. 1870, 9, 354) describe forms using only cold percolation and requiring the distillation to be done apart from the percolator; Schloesing (Ann. Chim. Phys. 1847, [3] 19, 239); Arnaudon (Il Nuovo Cimento, 1858, 8, 260); Gerber (Ber. 1876, 9, 656); Cazeneuve and Caillol (J. Pharm. Chim. 1877, [4] 25, 265); Tschlapowitz (Zeitsch. anal. Chem. 1879, 18, 441); Biechele (Correspondenz-Blatt des Vereins analytischer Chemiker, 2, 70); Wolff (*ibid.* 91); Guichard and Damoiseau (Répertoire de Pharmacie, 1880, 8, 97); Medicus (Zeitsch. anal. Chem. 1880, 19, 163); Thorn (Ger. Pat. 14523, 1880, and Dingl. poly. J. 1882, 243, 248; and with later improvements Ger. Pat. 18850, 1881, and Dingl. poly. J. 1882, 246, 374); Dunstan and Short (Pharm. J. 1883, [3] 13, 663); Kreusler (Chem. Zeit. 1884, 8, 1323); Thresh (Pharm. J. 1884, [3] 15, 281); Will (*ibid.* 363); Waite (*ibid.* 376); Johnson (Chem. News,

1885, 52, 39, and 82); Foerster (Zeitsch. anal. Chem. 1888, 27, 30, and 173); Neubauer (Dingl. poly. J. 1888, 267, 513); Lohmann (Chem. Zeit. 1905, 29, 365); Jackson and Zanetti (Amer. Chem. J. 1907, 38, 461), for small quantities of material—a little percolating tube is placed in the flask of solvent and under the end of the condenser.

The following are continuous infusion apparatuses:—

Scheibler's 2nd apparatus (Fig. 13).—As the first apparatus could not be constructed wider to hold large quantities without danger of the solvent percolating in one channel through the substance, and leaving part unextracted, Scheibler designed a modification involving continuous infusion with an overflow. The apparatus (shown in section in the figure) is made of metal, and the substance is placed in the innermost tube E, which is closed at the bottom with a piece of wire gauze with a layer of cotton

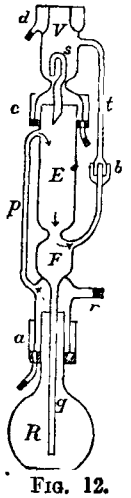


Fig. 12.

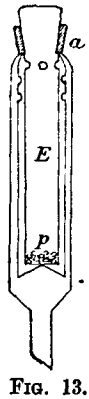


Fig. 13.

wool, *p*, above it. This tube slightly widens at the top and is ground into the top of the outer vessel so as to be removable. The outer vessel is composed of two tubes which are permanently united at the neck *a*; the outside one ends below in a funnel which fits into the vessel of solvent; the inner one is closed below, the bottom being bent up as shown; it has two rows of perforations in it near the top. The innermost tube has one row of perforations just below the neck. The vapours pass up the outer space and through the perforations to a condenser fitted to the neck of the innermost tube, the condensed liquid drops on to the substance, descends through it, then passes up the space between E and the next tube, and overflows through the lower row of perforations and so back into the vessel of solvent again (Ger. Pat. 9481, 1879).

Rempel's apparatus (Chem. Zeit. 1887, 11, 936) is also an overflow apparatus, but is so arranged that the substance is placed in the outside vessel and the liquid rises and overflows, and the vapours ascend through tubes in the centre.

Scheibler's 3rd apparatus (Fig. 14).—This was used in isolating vanillin from raw beetroot sugar. The substance to be extracted is placed in the vessel E (an elutriating vessel such as is used in the mechanical analysis of soils) and rests on a plug of cotton wool *b*. The solvent is

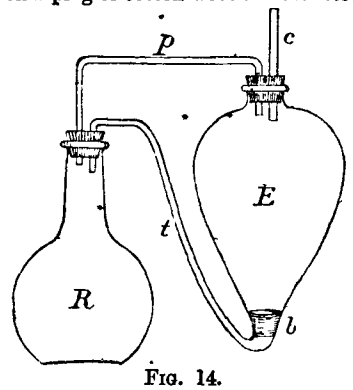


Fig. 14.

poured on to it, until some escapes from the tube *t* into the flask B which is placed on a water-bath. The vapours of the solvent are conducted by the tube *p* back into E, whence they pass through *c* to a reflux condenser. The condensed liquid flows back through *c* on to the substance in E, thus causing a constant overflow of liquid from the end of *t*, carrying with it the soluble constituents of the substance, which thus accumulate in B (Ber. 1880, 13, 338*a*).

References to other continuous infusion apparatuses are: Wynter Blyth (Chem. Soc. Trans. 1880, 37, 140); Johnstone (The Analyst, 1885, 10, 81); Stoddart (*ibid.* 108); Schmidt and Hänisch (Ger. Pat. 42753, 1887; and Dingl. poly. J. 1888, 268, 564); Koch (*ibid.* 1888, 267, 515); Landsiedl (Chem. Zeit. 1902, 26, 274), for use with solvents of either high or low boiling-point.

Intermittent infusion apparatuses are:

Simon's apparatus (Fig. 15).—Both the substance to be extracted and the solvent are placed

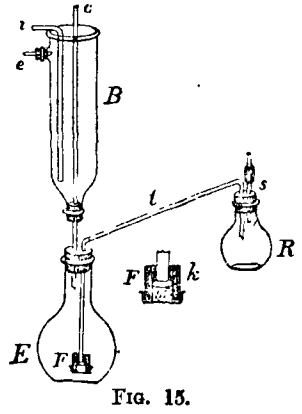


Fig. 15.

in the flask E, and are there heated together. The vapours ascend the tube *c* and are condensed by causing a current of water to circulate in the surrounding vessel B; the water enters through the tube *i*, and escapes by the tubulure *e*. A filtering apparatus, F, which is shown in section both in the flask and in the

enlarged figure at the side, is constructed by drawing a piece of flannel or fine linen over the end of the tube *t*, which passes for a little way into a perforated cork, *k*; another piece of flannel is tied over the lower end of the cork, and the space left between the two flannel surfaces is filled with some pulled-out wadding. The other end of *t* passes through a cork into the flask B, and through the same cork a short glass tube passes, to which is fitted, by means of a small cork, a short closed piece of glass tubing. When E has been heated for a time, *s* is opened by removing the small cork, with its closed tube, and the upper end of *c* is closed; then by means of an indiarubber tube attached to *i*, the water is siphoned out of the vessel B. The vapour of the solvent, being no longer condensed and being unable to escape, forces the solution up through *t* into the flask R, and the arrangement F filters it on its way. When no more passes over, C is opened and *s* is closed, the current of water is restarted in B, the source of heat is removed from beneath E, and the solvent is distilled from R back into E, leaving the dissolved matter behind in R. These operations are repeated until the substance yields nothing more to the solvent (Zeitsch. anal. Chem. 1873, 12, 179).

Auld and Pickle's apparatus (Fig. 16).—The substance to be extracted is placed, together with the solvent, in the large bolt-head flask E, which is heated in a water-bath. The vapours pass up the wide tube D, which is provided with a wide bore tap C, and are cooled by a reflux condenser attached to the top. *s* is a long tube ending in B in a small thistle funnel packed with cotton wool and covered with fine muslin or cotton cloth; the other end of *s* passes into the receiving flask R. A fairly wide tube, *t*, passes from the tube D at a point above the tap C down into the receiving flask R. When the solvent has become saturated, the tap C is closed for a moment, the pressure of the vapour then drives the solution through the cotton wool, and fills the tube *s*, which now acts as a siphon. The solvent is now boiled off from R, and passing up *t* is condensed and returned to E. The operation is repeated until the extraction is complete. With some solvents, a joint of wide indiarubber tubing can be used instead of the tap C, the tubing being pinched when it is desired to fill the siphon (Chem. News, 1909, 99, 242). The authors find that if the tube D is continued down into the flask E to a level a little above the thistle funnel, and is given a somewhat flanged termination, the apparatus will work automatically. When vapour is boiled off from R, it collects in D, forming a small column, which, when it has reached a certain height, forces the liquid into the siphon, which then empties E, and the process is repeated.

Schwaerzler (J. Pharm. Chim. 1853, [3] 24, 134) and Schiel (Annalen, 1858, 105, 257) have also described apparatuses in which the pressure of heated vapour is used to force the solution from one vessel to another.

References to other apparatuses of the intermittent infusion group are: Daubrawa (Vierteljahrschrift für practische Pharmacie, 1859, 8, 36); Fleury (J. Pharm. Chim. 1862, [3] 41, 282); von Schroeder (Zeitsch. anal. Chem. 1886, 25, 132); Barlow (Chem. News, 1888, 57, 56).

Soxhlet and Szombathy's apparatus (Fig. 17).—This was the first apparatus to introduce the use of the siphon to effect automatic intermittent infusion. The substance to be extracted, contained in a cartridge of filter paper, is placed in the wide tube E, at the bottom of which a tube, *s*, bent so as to form a siphon, is fused on. Another tube, N, not quite so wide as E, is fused on to the bottom of the latter, without, however, opening into it. The down tube of the siphon *s* passes through the side of N, and is sealed in by fusion. A reflux condenser is fitted to the top of E, and the tube N is fixed by a cork into a vessel of the solvent. On boiling the solvent, the vapours ascend through N and through the side tube *t*, which is sealed into both N and E, and

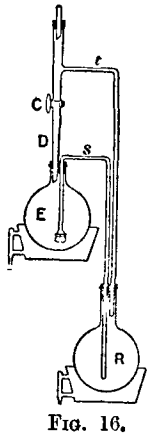


FIG. 16.

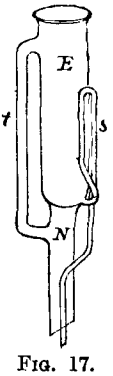


FIG. 17.

reach the condenser, whence the condensed liquid drops back into E and accumulates until it rises to the level of the top of the siphon *s*, when the siphon flows and empties the contents of E into the vessel beneath; E then fills again, and its contents are siphoned off every time the level reaches the top of the siphon tube. The top of the cartridge should be below the level of the top of the siphon, so that it may be completely immersed in the solvent, and it should rest on a plug of glass wool or strip of metal bent into a ring so that the opening to the siphon may not be closed (Dingl. poly. J. 1879, 232, 461).

Soxhlet and Szombathy's plan is now very widely adopted, and many variations of it have been devised. Lewkowitsch (Chem. Soc. Trans. 1889, 55, 359) attaches a tap to the siphon just before it enters the tube N in Fig. 17, so that a little of the solution can be drawn off to test the progress of the extraction. The siphon may be placed between the extracting vessel E and an outer vessel or inside the containing vessel; the risk of breakage is thus diminished, and the material and solvent are warmed by the ascending vapours. A trouble occurring in practice is that the large cork at the top, connecting the condenser to the apparatus, is apt to contain large pores that allow the vapour of the solvent to escape; several forms are arranged so as to avoid its use (Figs. 21, 22). The following are references and descriptions of various forms: Wollny (Zeitsch. anal. Chem. 1885, 24, 51); Thorpe and Robinson (Chem. Soc. Trans. 1890, 57, 41), a form made of

metal to hold 14 lbs. of bark; Buss (Chem. Zeit. 1903, 27, 813), a form made of metal for the hot extraction of several kilograms of material; Christ Kob & Co. (*ibid.* 1901, 25, 379), a form having a perforated glass plate fused in position just above the place where the siphon is attached to E in Fig. 17; Landsiedl (Chem. Zeit. 1902, 26, 274), forms for use with solvents of either high or low boiling-point.

Clausnizer and Wollny's apparatus (Fig. 18).—In this, the bottom of the inner tube E is drawn out, and to it a siphon tube is sealed on, as shown in the figure. The tube E and its siphon fit loosely into an outer tube, T, which is fitted into a vessel of the solvent below and leads

FIG. 18.

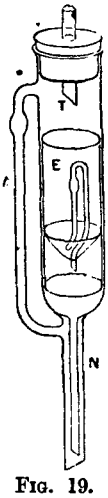


FIG. 19.

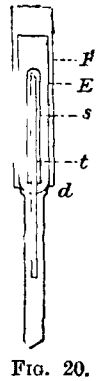


FIG. 20.

to a condenser above. The substance to be extracted is placed in E, and the mode of working is similar to that of the previous apparatus. The vapours passing up in the space between E and T maintain the substance and the solvent at a temperature approaching the boiling-point of the latter (Zeitsch. anal. Chem. 1881, 20, 81).

Frühling's apparatus (Fig. 19).—A cylindrical tube, E, resembling a tube for drying filters, is open at the bottom, but a little above the bottom it is closed by a conical diaphragm, through the apex of which passes the longer leg of a little siphon, which is thus held in position in E; it lies close to the side. This tube contains the material to be extracted, held in filter paper. The end of the siphon does not quite reach to the bottom of E, so that E can be placed upright on the balance pan, and weighed; it can be closed with a ground-in stopper during weighing. E is slipped into the outer tube T, closed by a glass stopper through which runs the tube of the condenser. The vapours of the solvent pass up the side tube *t*, are condensed, and the liquid when siphoned from E returns down the narrow tube in the interior of N (Zeitsch. angew. Chem. 1889, 242).

The feature of having the siphon inside the apparatus is adopted in the following forms: Sinnhold (Chem. Zeit. 1901, 25, 423): in this the vapour passes up a tube in the centre of a globular extraction vessel terminating below in a wide tube. The inner tube is ground into the wide tube, and has the siphon fused into it with the long leg passing down the centre, the bend and short leg being in the globular vessel. The apparatus is less fragile than other forms, and the inner tube and siphon can be removed in one piece for cleaning. Chatelan (Chem. Zeit. 1901, 25, 612) bends the delivery tube of the condenser slightly to one side, so that by twisting the condenser round, the solvent can be made to fall either on the material or into the orifice of a tube passing through the side of the extractor near the top. When in the latter position, the solvent is run off through a tap on the side tube, and the necessity is avoided of disconnecting the receiving flask and distilling off the solvent in a separate apparatus. Landsiedl (Chem. Zeit. 1902, 26, 275) describes forms for hot extraction. Rademacher (*ibid.* 1902, 26, 1177). Hesse (*ibid.* 1904, 28, 18) uses a cork in a tubulure at the bottom of the inner tube to hold the siphon in its place, thus making a very cheap form; the cork can be coated with chrom-gelatin.

King's apparatus (Fig. 20).—In this the siphon is differently constructed. Into the bottom of the wide tube E there is fused the long narrow tube *t*, which is ground off at an angle at its upper end. A tube, *s*, slightly wider than *t*, and closed at one end, is inverted over *t*, and rests on the upper end of the latter: it does not quite reach to the bottom of E. The tube E slips into a still wider one, F, which is dented in in several places at *d*, in order that the dents may support E and prevent it closing the narrower part of F. The substance to be extracted is placed in E, and rests on a plug of glass wool at the bottom. It is fitted up as in the two previous apparatuses, and when the liquid in E rises to the top of *s*, *s* and *t* form a siphon and draw off the liquid into the vessel below (Chem. News, 1888, 57, 235). Masojidek (Zeitschrift für Zuckerindustrie in Böhmen, 1881, 6, 51) and Boessneck (Chem. Zeit. 1887, 11, 1600) had previously described apparatuses on the same plan as King's. Thorpe and Robinson (Chem. Soc. Trans. 1890, 57, 44) employ an open topped bell-jar inverted with a siphon of this form to make a capacious apparatus.

In Jerwitz's apparatus and in Sanders's apparatus, the difficulty of the cork is avoided by causing the condensed solvent to enter the extracting vessel at the side instead of at the top; a light glass stopper can then be used to close the top of the extracting vessel, and the material undergoing extraction can easily be removed when extraction is complete, and fresh material introduced without disconnecting the condenser.

Jerwitz's apparatus (Fig. 21).—In using this the receiving flask F is attached to the bottom of the condenser and is held on by spiral springs. The cartridge of material to be extracted is placed in the extracting vessel A; ether is poured in up to the level E, and the vessel is closed by the glass stopper H, which is held in position by spiral springs. The tap B is then opened, and the ether is siphoned over into F. On heating F in a water-bath, the ether vapour ascends to K, and is there cooled by a current of water circulating in the outer space. The

condensed ether is prevented by the projecting tube J from flowing straight down into F, and is conducted through L into A, where it collects and is siphoned off intermittently through G. When the extraction is complete, the stopcock B is closed and the ether from F is driven off and collected in A. F is then removed, B is opened, and the ether is siphoned off into another vessel. The

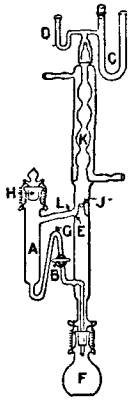


FIG. 21.

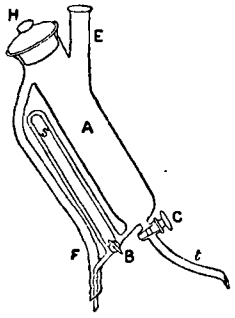


FIG. 22.

stopper H is then removed, and the cartridge of exhausted material is taken out by long tongs or a wire hook. At the top of the apparatus, a calcium chloride tube, C, prevents access of moisture to the ether, and the little tube D containing mercury and a plug of cotton wool acts as a safety valve should C get clogged (Chem. News, 1901, 83, 229).

Sanders's apparatus (Fig. 22).—In this apparatus, the material is placed in the extracting vessel A, which is closed by the glass stopper H and is held in a sloping position. The receiving flask containing the solvent is attached to the tube F, the taps B and C are closed, and on heating the flask, the vapours of the solvent pass up the tube F and through the upper part of A to the side tube E, which leads to a reflux condenser. When A is nearly filled with the condensed solvent, the siphon *s* discharges the solution into the receiving flask, and continues to work intermittently as in similar apparatuses. When the extraction is complete, the tap C is opened and the solvent is collected at the end of the tube *t*. If the tap B is left open during the operation, continuous percolation instead of intermittent infusion is effected. In a simpler form, the tap B and the cross-connection between the legs of the siphon are absent. The apparatus can be made on a large scale of tinned copper, the extracting vessel having the capacity of one litre (Chem. Soc. Proc. 1910, 26, 227).

Walpole (Chem. News, 1910, 102, 129) describes a form avoiding corks, and using only one joint and that a mercury joint.

Manufacturing Forms.

Roth's apparatus (Figs. 23 and 24).—This is employed for extracting oil from seeds by means of carbon disulphide. The solvent is stored in a reservoir, which is kept immersed in water to check evaporation. A pipe from an elevated water reservoir enters at the top of the carbon disulphide reservoir, and another pipe communicating with the extractor passes through the top of the reservoir and descends nearly to the bottom, so that when the tap of the water pipe is opened, the carbon disulphide is forced into the extractor. The latter is a cylindrical vessel, shown in section in Fig. 23; it is provided with a perforated false bottom, F, supported by struts G, G. The false bottom F is covered with sackcloth, and on it the ground seed or oil cake is placed and filled in up to another perforated plate, J, also covered with sackcloth. The top of the extractor is fastened on with screw clamps so as to be readily removable. At the bottom is a T-piece, communicating by the opening B with the carbon disulphide reservoir and, by the branch C, with a steam boiler. When filled and closed, carbon disulphide is forced in through B, and when it has dissolved the oil, fresh carbon disulphide is forced in at B, causing the first charge to overflow down the pipe L, the entrance to which is protected with a strainer, and to pass to the distilling apparatus. A gauge, Q, shows the level of the liquid, and also allows samples to be drawn. The material is treated some three times or so with the fresh solvent until a sample taken at Q is found to be free from oil; half of the last charge is then conducted through the tap E, and a pipe connected with it to another similar extractor, and the other half is returned to the carbon disulphide reservoir. In order to recover the last portions of solvent adhering to the material, the valve N is opened and steam is sent in through C; the carbon disulphide is thus boiled off and passes through N to a con-

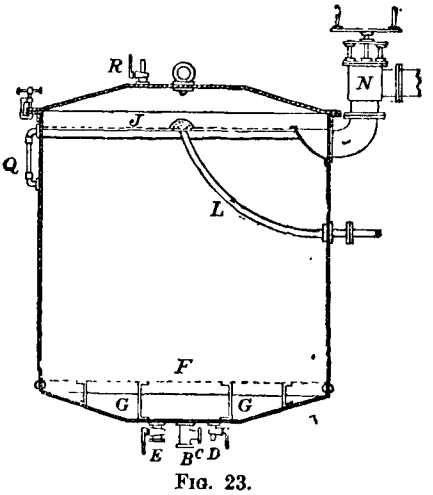


FIG. 23.

denser. When all carbon disulphide is driven off, the taps R and D are opened; the former allows the steam to escape and the latter allows the condensed water to run off. The cover is then removed and the extractor is emptied and refilled with fresh material.

The distilling apparatus, shown in section in Fig. 24, is a cylindrical vessel, into which the solution of oil is introduced through the tap E and pipe attached which descends nearly to the

bottom. The vessel is half filled with liquid, the level being ascertained by the gauges F, F. At the bottom of the vessel are two steam coils;

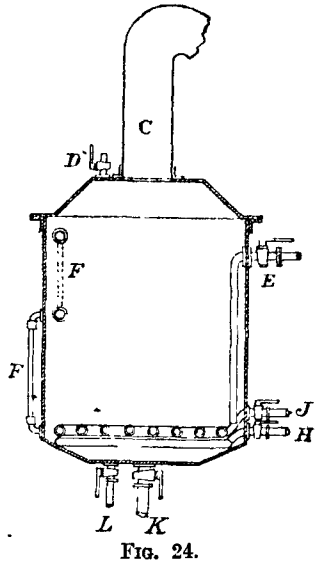


FIG. 24.

the lower one is perforated with a number of small holes and is fed by the tap H; the upper one is not perforated, and is fed by the tap J, and the condensed water from it escapes through the tap L. At first, steam is slowly passed through the upper coil and heats the carbon disulphide, the vapours of which pass by the wide tube C to a special form of condenser; when nearly all the carbon disulphide has escaped, steam is passed through H, and, escaping by the perforations through the oil, removes the last traces of the solvent. The tap D allows the steam to escape at the end of the distillation. The oil is finally run off through the tap K to a reservoir, where it is allowed to stand until the condensed water has separated in a layer (Schaedler's Technologie der Fette und Oele, 1883, i. 292).

Leuner's apparatus (Fig. 25).—This is employed for removing fat from bones. The bones are filled into the cylindrical vessel A (shown in section in the figure), and rest on the perforated false bottom *aa*; then all the taps are closed except *p*, and steam is injected through the pipe *b*; when all the air is expelled, *p* is closed, and the bones are kept in contact with steam under pressure for a time. Steam is then shut off, and the taps *p* and one attached to the tube *d* are opened, and the condensed water is drawn off. In the cylindrical vessel B there are placed equal volumes of water and petroleum naphtha or other volatile solvent; taps *p* and *d* are closed, and taps *g* and *i* are opened, as also are the taps *q* and *r*, to allow the water and solvent to flow into A; *q* and *r* are then closed, and an equal volume of water is introduced into B. Steam is now passed through the pipe *cc*, and this heats the water which forms the lower layer in A, and the heat is communicated to the upper layer of solvent. The vapours rise through the bones and pass through the pipe *ss* to the small vessel C, and thence to the reflux condenser contained in D. The condensed liquid collects in C until it reaches the opening into *s*, when it flows back into A and is spread over the bones by the arrangement shown at the top. Any vapours that are not condensed pass through the pipe *l*, and are led under the surface of the water in B, which is provided with a small condenser E to prevent the escape of vapours of the solvent to the air. The bones are thus subjected at the same time to the action of steam and petroleum vapour and also of liquid petroleum. After this action has gone on for some time, the tap *g* is closed and *h* is opened; the vapours evolved from A then pass to a second condenser, which is contained in D and communicates with C—it is indicated by dotted lines—and the tap *k* is opened; this allows the solvent to flow

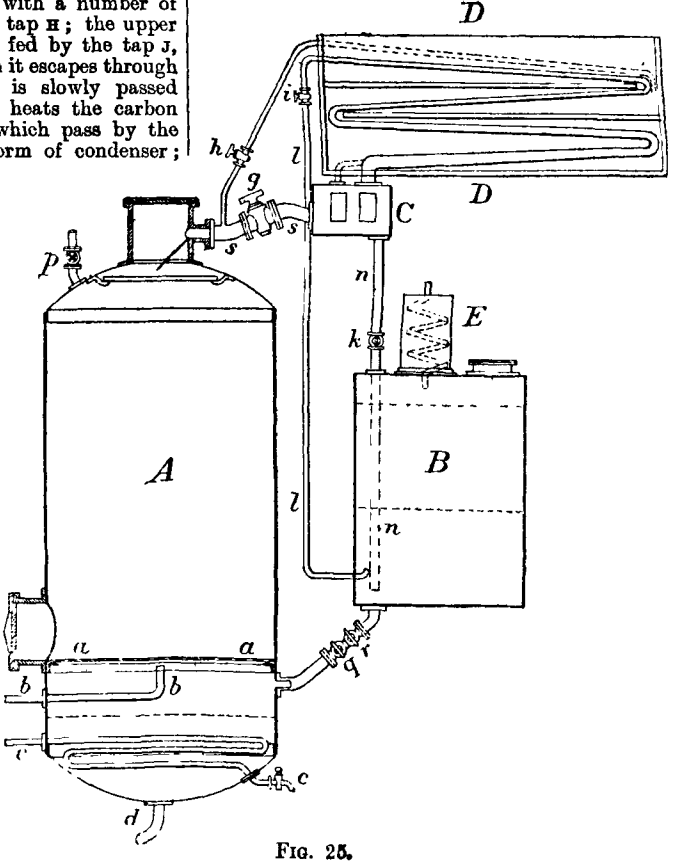


FIG. 25.

from C down the tube *nn* and collect in B. The heating is continued until all the solvent is driven off and water only enters C: this can be seen by glazed apertures in that vessel. When this occurs, the operation is finished, and a mixture of fat and of aqueous liquid is drawn off by the pipe *d*, and the latter is used in preparing glue (Ger. Pat. 17181, 1881, and J. Soc. Chem. Ind. 1882, 1, 155).

Merz's apparatus (Fig. 26).—This apparatus is designed for the extraction of various sub-

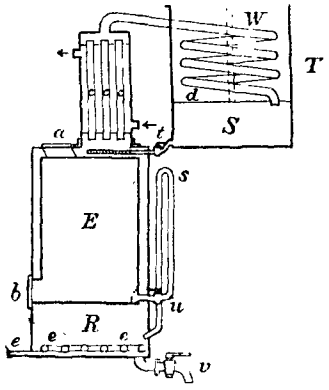


FIG. 26.

stances with volatile solvents; it can also be used with animal charcoal for decolourising purposes. It consists of an inner vessel, E, which is open at the top and is contained in a closed outer vessel B. The substance is filled into E through the manhole *a*, and at the end of the operation it is removed through the manhole *b*. The solvent is stored in a reservoir S, which forms the lower part of the condensing vessel T, and is divided from the upper part by the partition *d*. The extractor E is filled with solvent by opening the tap *t*. When the level of the liquid rises as high as the top of the siphon *s*, the latter begins to act and runs off the liquid from E into the outer vessel B. The entrance to the siphon is protected by the sieve arrangement shown at the bottom of E. Steam is made to circulate through the coil *eee* at the bottom of B; this causes the solvent to boil, and its vapours circulate in the space between B and E, warming the latter and its contents, and then pass to the condensing tubes *c*, *c*, *c*, round which water is circulating. The condensed liquid falls back into E, and when the level again reaches that of the top of the siphon the siphoning-off is repeated and so on over and over again. The substance is thus submitted to intermittent infusion. Samples can be drawn off at *u*, and when the extraction is found to be complete, the water that surrounds the tubes *c*, *c*, *c* is withdrawn. The solvent then boils off, and after condensation in the worm W returns to the reservoir S. The extract is drawn off by the tap *v*. By regulating the tap *u*, the substance can be made to undergo continuous instead of intermittent infusion, if desired (Ger. Pat. 20742, 1882, and J. Soc. Chem. Ind. 1883, 2, 234).

The extraction of the volatile oils to which the odour of flowers is due, forms an important industry; the apparatus employed is simple in principle, the only complexity being in the arrangement of the battery of extracting vessels, reservoirs of solvent, and stills (*see* Gildemeister, Die Ätherischen Öle, 2d. ed. 1910, 266). *Garnier's apparatus* (Figs. 27, 28, and 29), however, presents some novelty; it consists of a cylinder, C, revolving on a horizontal axis inside a cylindrical vessel, V; the end plates E, E of the revolving cylinder present a number of circular rings (Fig. 28), each of which is united to the corresponding ring at the other end by a number of rods forming an open framework (Fig. 29). Into the frames formed by the rods long cylindrical baskets B, B of open work containing the flowers can be thrust through a manhole, M, at the end of the cylindrical vessel. When all the baskets are in position, the manhole is closed, and enough solvent is introduced through F to cover the lowest basket. The cylinder is then made to revolve, and thus one basket of flowers after another is immersed in the solvent; as the cylinder has no outer wall, the solvent can move freely through the baskets. Heat can be applied by passing steam through the spiral pipe PP, and the vapours of the solvent pass by the still head S to the condenser K. When extraction is complete, the solution is drawn off by the tap T. At the end of the operation, steam can be blown into the apparatus through the tap U, and the last remnants of the solvent can thus be driven off and condensed in K. By this apparatus, many baskets of flowers can be extracted by the same comparatively small quantity of solvent (Fr. Pat. 1904, 342534; Gildemeister, *l.c.* 271).

Liquids. A substance held in solution by a

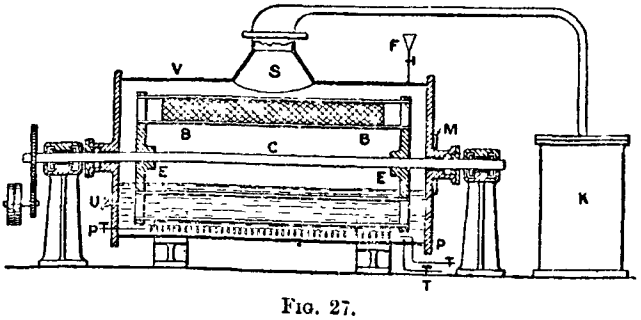


FIG. 27.

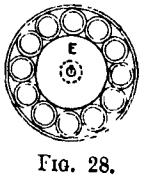


FIG. 28.

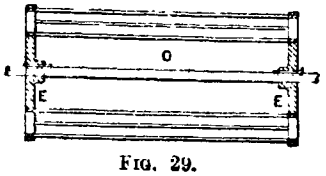


FIG. 29.

liquid can often be removed by treating the liquid with a solvent that is not miscible with it. The ordinary procedure is to shake the liquid and the solvent vigorously together in a separator, which is a pear-shaped or cylindrical glass vessel terminating in a stoppered tubulure at its broad or top end, and in a stopcock and short tube at its narrow or lower end. After shaking, the vessel is allowed to stand until the liquid and the solvent have separated into two layers. The stopper is then removed, and the lowermost layer tapped off by means of the stopcock and tube. This treatment is repeated with fresh solvent until the liquid has given up all the dissolved substance it contained.

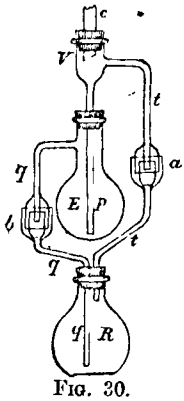


FIG. 30.

Schwarz has invented an apparatus which works automatically and avoids the tedious operations of the old method.

Schwarz's apparatus (Fig. 30).—The liquid from which the substance is to be extracted is placed in the flask E, and the solvent, which must be lighter than the liquid, is placed in the receiving flask R, and is there boiled. The vapours ascend through the tube *t* to the upper vessel V, and thence through the tube *c* to a reflux condenser. The condensed solvent descends the tube *p*, then rises through the liquid in E, and collects as a layer above it until it reaches the opening into the side tube *q*, when it overflows and returns to the flask R. This circulation goes on automatically, and when on testing a drop of the overflowing liquid, the extraction is found to be complete, water is poured down V until all the solvent overflows down *q* into R; the parts are then disconnected, E is emptied, and by reconnecting and heating R, the solvent can be distilled off into E, leaving the desired substance in R. At *a* and *b* are mercury joints, which enable connection and disconnection to be readily made (Zeitsch. anal. Chem. 1884, 23, 368).

The following are references to other apparatuses for extracting liquids. When the solvent is heavier than the liquid: Pregl (Zeitsch. anal. Chem. 1901, 40, 785) and Baum (Chem. Zeit. 1904, 28, 1172), these are of simple construction, and adapted for extracting aqueous liquids with chloroform; Lentz (Chem. Zeit. 1901, 25, 820), for use with chloroform, it can be easily fitted up with ordinary laboratory apparatus; Stephani and Böcker (Ber. 1902, 35, 2698), it can also be used for solids. When the solvent is lighter than the liquid: Neumann (Ber. 1885, 18, 3061); Elloart (Chem. News, 1886, 53, 281); Tcherniak (Ber. 1892, 25, 3650); Pip (Chem. Zeit. 1903, 27, 706); Pelizza (*ibid.* 1904, 28, 186); Bowman (Chem. Soc. Proc. 1906, 22, 24). When the solvent is either heavier or lighter than the liquid: Wollny (Zeitsch. anal. Chem. 1885, 24, 52); Grauer (Dingl. poly. J. 1886, 262, 475), forms on a manufacturing scale; Hagemann (Ber. 1893, 26, 1975); Landsiedl (Chem. Zeit. 1902, 26, 274).

H. H. R.

F

FACTIS (*Faktis, Factice, Parafactis*). A general term applied to so-called rubber substitutes prepared from oils.

White substitute is made by stirring sulphur monochloride into linseed, rape-seed, refined colza oil, or other unsaturated oil with or without admixture of petroleum spirit. A considerable rise of temperature occurs; the oil thickens, and, when the reaction has proceeded far enough, the whole is poured into trays, and solidifies to an elastic solid, somewhat resembling rubber. It is necessary to control the temperature, and therefore only limited charges of material are used.

The product is an additive compound of the oil and sulphur monochloride, and consists mainly of the glycerides of fatty acids containing chlorine and sulphur (Ulzer and Horn, Jahresb. Chem. Technol. 1890, 1177; Henriques, Chem. Zeit. 1893, 707).

Dark or French substitute is obtained by heating a vegetable oil to 200°, and stirring in sulphur. The liquid thickens, and on cooling solidifies to a black elastic solid. It is sometimes prepared from rape-seed oil or cotton-seed oil which has previously been partially oxidised by treatment with air at a high temperature (*v., e.g.*, Eng. Pat. 15163, 1899). Substitutes manufactured from these 'blown oils' have a sp.gr. less than 1, and are accordingly known as 'floating substitutes' (*v.* Altschul. Zeitsch. angew. Chem. 1895, 535).

A wet method of manufacture consists in oxidising the oil with dilute nitric acid at 100°, and then adding colophony, spirit of turpentine, sodium chloride, and sodium polysulphide, and boiling till the factis has the proper consistency. It is then finally washed, dried, and rolled (*v.* Lutenaf. Rev. Prod. Chim. 3, 147; J. Soc. Chem. Ind. 1900, 673).

The cost of manufacture of factis averages less than 7*d.* per lb. and by the use of maize oil may be brought as low as 3*d.* per lb. These preparations, however, have only a limited application as rubber substitutes because of their small elasticity and insolubility in the usual rubber solvents. Also they are easily hydrolysed by steam and other agents. If excess of oil and sulphur are first removed from the factis by treatment with carbon disulphide, acetone, &c., they may be incorporated with a proportion of pure rubber, and their usefulness much increased (Ditmar, Fr. Pat. 377538, 1907; J. Soc. Chem. Ind. 1907, 1058; *v. also* Chercheffsky, D. R. P. 218225, 1908; J. Soc. Chem. Ind. 1910, 440; and Heil and Esch, Manufacture of Rubber Goods, 110).

FAHLORE. A partial translation of the old

German name *Fahlerz*, applied, like the term 'grey-copper-ore,' to minerals of the tetrahedrite group. These are essentially sulphantimonites or sulpharsenites of copper with the general formula $R'_3R'''S_3$, where R' represents copper and silver, and R''' antimony, arsenic, or, exceptionally, bismuth. In many instances, however, small amounts of iron and zinc (less often mercury, lead, or cobalt) are also present, and the formula then becomes

$$R'_3R'''S_3+n(6R''S\cdot R'''_2S_3),$$

where R'' represents iron, &c., and n is a small fraction usually $\frac{1}{10}$ or $\frac{1}{3}$ (Prior and Spencer, Mineralog. Mag. 1899, xii. 202). Owing to this wide range of isomorphous replacement, the actual composition of fahlore is extremely variable, as is illustrated by the following analyses. Further, owing to the fact that fahlore usually forms intimate intergrowths with other minerals, more particularly copper-pyrites, it is probable that many of the older analyses were made on material which was not ideally pure :—

——	I	II	III	IV	V	VI
S .	24·48	24·38	23·15	27·60	21·17	22·96
Sb .	28·85	28·32	27·73	—	24·63	21·35
As .	trace	trace	trace	19·04	—	—
Bi .	—	0·83	—	—	—	—
Cu .	45·39	41·55	30·56	49·83	14·81	34·57
Ag .	—	—	15·26	1·87	31·29	—
Fe .	1·32	1·02	3·51	1·11	5·98	2·24
Zn .	—	2·63	trace	—	0·99	1·34
Hg .	—	—	—	—	—	15·57
Pb .	0·11	0·62	0·05	0·17	—	—
	100·15	99·30	100·26	99·62	98·87	98·03
Sp.gr.	4·921	4·969	5·047	4·62	—	5·107

I, Tetrahedrite from Fresney d'Oisans, Isère, France (G. T. Prior, 1899); II, tetrahedrite from Horhausen, Rhenish Prussia (G. T. Prior, 1899); III, tetrahedrite from Wolfach, Baden (G. T. Prior, 1899); IV, tennantite ('binnite') from Binnenthal, Switzerland (G. T. Prior, 1899); V, argentiferous tetrahedrite (freibergite) from Freiberg, Saxony (H. Rose, 1829); VI, mercurial tetrahedrite (schwartzite) from Schwarz, Tyrol (Weidenbusch, 1849).

Many of the names which have been applied to the minerals of this group express these differences in composition. Tetrahedrite (Fr. *Panabase*) and tennantite denote the antimonial and arsenical series respectively, and these are usually regarded as species; other names take the rank of varieties under these. For example, freibergite (Ger. *Weissgiltigerz*) is a variety of tetrahedrite containing much silver; schwartzite is a mercurial tetrahedrite; and malinowskite one containing lead. In the arsenical series, or tennantite, the names sandbergerite and kupferblende are applied to varieties rich in zinc; rionite and annivite to those containing bismuth.

Although differing so widely in chemical composition, all varieties of fahlore are identical crystallographically, the type of symmetry being that of the tetrahedral class of the cubic system. A pronounced tetrahedral habit of the crystals is extremely characteristic of the antimonial members (hence the name tetrahedrite), whilst in the arsenical series (tennantite) this is often somewhat masked by the greater development of the rhombic dodecahedron. The colour is iron-black to steel-grey, and the lustre metallic and often brilliant. The fracture of pure material is typically conchoidal, with a brilliant lustre. The streak is usually black, but in some specimens (those containing but little iron) it is dark reddish-brown; hardness, 4; sp.gr. 4·4–5·1.

Fahlore occurs in mineral-veins in association with other metallic minerals. Beautifully crystallised specimens have been found in many mining districts, notably at the Herodsfoot Mine near Liskeard in Cornwall, Clausthal in the Harz Mountains, Kapnik in Hungary, &c. In the massive condition it is, at times, found in some abundance, *e.g.* in Nevada and Utah, and it is then an important ore of copper. The bulk of the rich silver ores of Bolivia consist of argentiferous tetrahedrite. L. J. S.

FARINA, or POTATO STARCH. The starch of the potato, *Solanum tuberosum* (Linn.). The tubers are placed in a cylinder furnished with teeth by means of which the starch cells are lacerated whilst the mass of potatos is reduced to a stiff pulp. The starch granules are washed out and allowed to settle in vessels of water, when the water is drawn off. The moist starch, after being separated from the cellulose, is dried and broken up between iron rollers. It is then ready for its purpose, which is in the main the sizing of textiles.

As a material for the purpose of sizing, farina produces when boiled a thicker paste than any other starch; consequently, a small amount of it will furnish a liquor of the same density as a much larger quantity of, for instance, wheaten flour. On the other hand, the starch cells of the potato being exceptionally large, a certain amount of coarseness is felt in cotton goods stiffened by it. For this reason, it is seldom used with China clay alone, but is usually mixed with a greater or smaller proportion of flour. It is claimed for farina that, since the potato contains a small amount of nitrogenous matter, it is not so prone to induce mildew in cotton goods as are other forms of starch.

Farina has a glistening appearance and a crisp feeling when pressed between the fingers. It contains a larger proportion of moisture than any other starch, varying from 17 to 20 p.c. The granules are very characteristic, being for the most part large, though irregular in size, and resembling an oyster-shell in form, being, moreover, marked with similar eccentric rings.

The following is the average composition of ordinary commercial farina :—

Water	16·72
Cellulose	0·36
Ash	0·22
Starch	82·70
	100·00

Farina is preferred to other starches for the manufacture of British gum, its great purity making it especially suitable for this purpose (*v.* STARCH).

FARNESOL, an alcohol found by Haarmann and Reimer in the oil of quassia flowers. It is

found also in Peru and tolu balsam and palmarosa oil, and also, by Elze (Chem. Zeit. 1910, 34, 857), in cananga oil from Java. It is optically inactive; sp.gr. 0·985 at 15°, and boils at 145°–146° at 3 mm.

FAST ACID FUCHSIN, -SCARLET *v.* AZO-COLOURING MATTERS.

FAST-BLACK, -GREEN M *v.* OXAZINE COLOURING MATTERS.

FAST BLUES *v.* INDULINES.

FAST BORDEAUX *v.* AZO- COLOURING MATTERS.

FAST BROWN N, ACID BROWN, NAPHTHYLAMINE BROWN *v.* AZO- COLOURING MATTERS.

FAST COTTON BLUE, -BROWN *v.* AZO-COLOURING MATTERS.

FAST PONCEAU B and **2B, BIEBRICH SCARLET, PONCEAU 3R** or **3R B,** *v.* AZO-COLOURING MATTERS.

FAST REDS or **ROCELLIN, RUBIDINE, ORSEILLINE** *v.* AZO- COLOURING MATTERS.

FAST SCARLET *v.* AZO- COLOURING MATTERS.

FAST SULPHONE VIOLETS *v.* AZO- COLOURING MATTERS.

FAST YELLOW *v.* AZO- COLOURING MATTERS.

FAT LUTE *v.* LUTES.

FATTY ACIDS. A numerous and important group of acids of the general formula $C_nH_{2n}O_2$, certain members of which are essential constituents of the animal and vegetable fats. The lowest term of the series is formic acid H·COOH; the highest term at present known is dicetylic acid $C_{34}H_{68}O_2$. As the radicle C_nH_{2n+1} may exist in at variety of modifications, it follows that the fatty acids are also capable of existing in numerous isomeric forms. The fatty acids may, like the monovalent alcohols, be distinguished as primary, secondary, and tertiary. The secondary acids are usually termed *iso-acids,* whilst the acids containing the groups $CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}$ . . . are called *normal acids.*

The naturally occurring fatty acids are found partly free and partly in the form of esters. Formic acid is found in ants, caterpillars, and in the stinging-nettle; butyric acid in butter, in perspiration, and, combined with hexyl alcohol, in the fruit of *Heracleum villosum* (Fisch.); cerotic acid in bees-wax; stearic acid in animal fats, &c. The higher members of the series, in combination with glycerol, forming the so-called *glycerides,* constitute the greater part of the more important animal and vegetable fats and oils and the different varieties of the waxes.

The lower members of the series, formic, acetic, propionic acids, etc., are mobile volatile liquids, miscible with water, alcohol, and ether in all proportions. As the number of carbon atoms increases, they become less soluble in water, more oily and viscid, and less volatile. Thus nanthylic (*heptoic*) acid $C_7H_{14}O_2$ is insoluble in water; capric (*decylic*) acid $C_{10}H_{20}O_2$ is solid at ordinary temperatures; whilst lauric acid $C_{12}H_{24}O_2$ and the higher homologues cannot be distilled under ordinary pressure without decomposition.

The most important general methods of obtaining these acids are:

(1) By the oxidation of the primary alcohols or aldehydes, *e.g.* ethyl alcohol → acetic acid.

(2) By the addition of hydrogen to the unsaturated monocarboxylic acids, *e.g.* acrylic acid → propionic acid.

(3) By the reduction at high temperatures of hydroxy-acids with hydriodic acid or of halogen substituted acids with sodium amalgam, *e.g.* α-hydroxypropionic acid → propionic acid.

(4) By heating the acid nitriles with acid or alkali, *e.g.* acetonitrile → acetic acid.

(5) By decomposing ketones through oxidation with potassium permanganate, *e.g.* pentadecylmethylketone (obtained from palmitic acid) → pentadecylic and acetic acids.

(6) By decomposing unsaturated acids by fusion with caustic potash, *e.g.* oleic acid → palmitic and acetic acids.

(7) By decomposing the mono- and dialkyl-acetoacetic esters with concentrated potash solution, *e.g.* diheptylacetoacetic ester → diheptyl-acetic acid.

(8) By heating dicarboxylic acids, in which the two carboxyl groups are in union with the same carbon atom; *e.g.* dicetylmalonic acid → dicetylic acid.

The more important transformations which the fatty acids can be made to undergo are as follows:—

(1) Acids and alcohols yield *esters* in the presence of hydrochloric or sulphuric acids.

(2) The halogens react, producing substitution products.

(3) Acids or their salts, when acted on by the chlorides of phosphorus, yield *acid chlorides* and *acid anhydrides.*

(4) The ammonium salts of the acids split off water and become *acid amides* and *acid nitriles.*

(5) *Primary amines* are produced by the reduction of the acid nitriles and by the action of bromine and sodium hydroxide on the acid amides. In the latter case, carbon dioxide is evolved and the primary amine of the next lower acid is produced.

(6) When the calcium salts are distilled with calcium formate, *aldehydes* are produced, but, when distilled alone, the calcium salts yield *ketones.*

(7) *Paraffins* are produced by the reduction of the higher fatty acids with hydriodic acid, by the electrolysis of concentrated solutions of the potassium salts of the acids and by the distillation of the calcium salts with soda lime.

The various members of the fatty acid series are described under their separate headings.

FAVERSHAM POWDER *v.* EXPLOSIVES.

FAVIER'S EXPLOSIVE *v.* EXPLOSIVES.

FAYENCE *v.* POTTERY and PORCELAIN.

FEATHER-ALUM. A name (Ger. *Federalaun*) applied by Klaproth in 1802 to the iron-alum ($FeSO_4{\cdot}Al_2(SO_4)_3.24H_2O$) now known as halotrichite. Like alunogen (*q.v.*), kalinite (potash-alum), pickeringite (*magnesia-alum*), &c., it occurs as a delicately fibrous efflorescence on shale and some other rocks; and it is possible that these species also may have at one time or another been included under the indefinite term 'feather-alum.' L. J. S.

FEATHER-ORE. A popular term (Ger. *Federerz*) applied to a number of finely fibrous minerals, which possess in common a lead-grey colour with metallic lustre. The material forms delicate tufts or felt-like masses. Brittle 'feather-ore' is referable to jamesonite (*q.v.*), since this possesses a good cleavage perpendicular

to the length of the fibres. On the other hand, flexible 'feather-ore' may be stibnite (Sb_2S_3), plumosite ($2PbS{\cdot}Sb_2S_3$), or one of the several other fibrous sulphantimonites of lead (Spencer, Min. Mag. 1907, 14, 207). L. J. S.

FECULOSE is the term by which the various commercial starch esters are designated. They are best formed by the action of glacial acetic acid on starch, and then washing the product with cold water to free it from uncombined acid. By varying the starch base and the time and temperature of the reaction, or the concentration of the acid, an endless variety of products may be obtained according to the purpose for which they are required.

Feculose differs little in appearance or in ordinary chemical properties from ordinary starch. On boiling with water, it gives a clear homogeneous solution which does not set or revert on standing, gives the usual blue colour with iodine, and does not reduce Fehling's solution. When a little of the solution is allowed to dry on a clean glass plate, it forms a clear flexible film equal to that of the finest gelatin. The washed feculose is neutral or slightly acid, and reacts with most chemical reagents more readily than ordinary starch.

Uses.—Feculose has been described as an ideal substitute for gelatin and vegetable gums. It has been applied as a special textile finish to confer lustre and substance to textiles in the form of yarn or cloth and also as an excellent dressing for linen, lace, and silk. It is also employed in dyeing and French cleaning; in confectionery for making jujubes and other sweets, and in paper coating as a size in place of 'chromo' glue or casein. The surface produced in the latter case has excellent printing qualities.

A permanent solution of feculose can be obtained by varying the original process of manufacture, and by various subsidiary treatments it can be made to fulfil a large range of technical requirements (Traquair, J. Soc. Chem. Ind. 1909, 288; Farrell, J. Soc. Dyers, Dec. 1908).

FEEDING STUFFS. Under this head will be considered the principal articles in use as food for live stock.

The main constituents of feeding stuffs, apart from water, are (1) nitrogenous bodies, subdivided into albuminoid or proteid substances and non-albuminoid bodies, such as amides; (2) oil or fat; (3) carbohydrates, including easily digestible substances like sugar or starch, and indigestible or less easily digestible bodies of the cellulose type; (4) the so-called 'mineral' constituents which constitute the 'ash' left on incineration. There are also frequently present other bodies, such as resinous matters, colouring matters, enzymes, and traces of glucosides and organic bases of the alkaloidal type; but these exist in relatively small quantities, and are usually ignored in commercial analyses. Small quantities of neutral or acid organic salts are also found in roots and green fodder crops.

Albuminoids or Proteins. These are bodies having the general chemical constitution of highly complex amino-acids. There is a large variety of proteins, and various distinct compounds of this type probably coexist in most foods, while many well-defined types are present in some foods and lacking in others. The albuminoids of wheat, for example, have properties which sharply distinguish them from those of other cereals such as barley, oats, or maize, and the albuminoids of the leguminous grains differ from those found in any of these. The detailed study of the albuminoids has recently engaged much attention at the hands of physiological chemists, and it appears probable that further study will throw light on much that is obscure as to the relative feeding value for different purposes of albuminoids derived from different sources, and may afford an explanation of the practical experience which shows that a mixed diet is often productive of better results than a simpler diet which may supply the same aggregate quantity of nitrogenous matter. Albuminoids consist of carbon, hydrogen, oxygen, nitrogen, and a small quantity of sulphur. On the average, they contain 16 p.c. of nitrogen, and are usually calculated from the nitrogen present on this assumption. In some foods (see *infra*) the proportion of non-albuminoid nitrogenous compounds is sufficient to make it desirable to separate these in analysis, and to calculate the albuminoids from the true proteid nitrogen only. But in most concentrated foods it is conventional and sufficiently near for practical purposes, to calculate the albuminoids by multiplying the total nitrogen present by 6·25.

The chief function of albuminoids in food is to build up the nitrogenous tissue of the growing animal, and to replace the daily nitrogenous waste due to the normal processes of metabolism. Hence they have long been called 'flesh-formers,' in contradistinction to fat and carbohydrates. Albuminoids, however, are also capable of being partially transformed into fat, and also of generating heat and motive energy by their oxidation. These functions, however, are mainly performed by fat and carbohydrates.

The digestion of albuminoids is effected mainly by the action of pepsin, secreted by the stomach, and of trypsin, which is a constituent of the pancreatic juice. By these ferments, they are converted into soluble bodies, peptones and albumoses, which are then absorbed into the animal system.

The non-albuminoid nitrogenous constituents of food, chiefly amides, are soluble and need no digestion. They do not form muscular tissue, like the albuminoids, but they yield heat and energy, and to some extent help to preserve the nitrogenous constituents of the body itself from waste.

Oil or Fat. A large number of fats are found in vegetable tissue. For the main part they are triglycerides of one or other of the series of bodies known as the 'fatty acids'; but they also include in some cases small quantities of wax or fat in which the glyceryl radical is replaced by that of some solid alcohol like phytosterol. Lecithin, which is present in small quantities in some vegetable substances, is a fat containing nitrogen and phosphorus. In the analysis of feeding stuffs, the matter extractable by ether is usually assumed to be fat, though in the case of some foods small quantities of resinous bodies are included in the extract, as well as chlorophyll.

The function of fat as a food is to build up

the fat of the body and to furnish heat and energy on its oxidation or combustion in the blood.

Fat is digested and rendered absorbable into the blood mainly by the action of bile, aided by the pancreatic secretions and those of various intestinal glands.

Carbohydrates. Sugars of various types occur in feeding stuffs, sometimes in insignificant quantity, as in ordinary grain, sometimes in large quantity, as in some roots, the feeding value of which lies principally in these constituents. Thus mangolds and beets contain sucrose or cane sugar, whilst turnips contain dextrose or 'grape sugar.' In addition to sugars of the hexose type, some fodder plants yield sugars of the pentose type. Sugars, being soluble, need no 'digestion.'

Starch, which is practically perhaps the most important of the carbohydrates, consists of organised cells which are insoluble in cold water though capable of being gelatinised and partially dissolved by boiling water. Starch is convertible by mineral acids into sugar (dextrose), and is resolved by certain ferments, both vegetable and animal, into the soluble bodies maltose (malt sugar), and dextrin, a viscous body devoid of sweetness. The latter resolution is effected by the ferment *ptyalin* in the saliva, and also by a ferment contained in the pancreatic juice. The acid secretions of the stomach also act on starch, and the maltose and dextrin are further modified into dextrose during passage through the intestines.

Cellulose. Numerous substances are grouped under this head. The typical form of cellulose is cotton. Material of this nature forms the coating of vegetable cells, and consequently the whole 'skeleton' of a plant. But it is modified in composition in different tissues, and sometimes partially assumes a woody form, as in straw and hay. In food analyses, the various forms of cellulose are called 'fibre,' and are determined by boiling the food successively in weak mineral acid and weak alkali, and extracting with alcohol and ether. The residue is usually described as 'fibre' or 'crude fibre,' or sometimes as 'indigestible fibre.' The last description was given on the assumption that the artificial digestion referred to was equivalent in ultimate effect to the digestive processes of the animal. But modern research has shown that bodies of the cellulose type which resist the solvent treatments referred to are to a variable extent partially digestible, especially by ruminants. This digestion is probably mainly effected by the action of bacteria in the large intestine. A ruminant can digest much more cellulose than a horse, and a horse much more than a pig. The very thorough mastication of the ruminant better prepares the fibre for such digestion as is possible than does the imperfect mastication of the horse or the still more imperfect mastication of the pig, apart from the anatomical differences in the digestive tracts of the respective animals and the relative abundance of bacteria capable of effecting cellulose digestion. How much the physical or mechanical condition of the fibre has to do with its digestion has been demonstrated by Kellner, who found that, when straw fibre was disintegrated by boiling with soda lye under pressure (as in the preparation of fibre for paper making), the fibre had a digestibility coefficient of 56 to 60 p.c., whereas, in the unprepared straw, it was only 42 p.c.

Other insoluble carbohydrates are those of the pentosan type, which yield pentose sugars on treatment with acids, but the conditions affecting their digestion are not well understood, and the feeding value of the pentoses which they yield is probably small.

The function of carbohydrates is to supply the main quantity of fuel for the generation of heat and the production of mechanical force, and, when these necessary requirements are fulfilled, the excess serves to build up fat in the body.

Mineral matters, or 'ash constituents,' are the residues left on incineration of the heterogeneous mass of organic compounds and salts contained in the food. Probably most of the 'mineral' matter thus obtained exists in the food in organic combination. The chief constituents of the ash are phosphoric acid, sulphuric acid, calcium, potassium, and magnesium, with smaller quantities of iron, sodium, and chlorine, and traces of fluorine. Silica is also a large constituent of straw, and is found in grass. Other elements are no doubt commonly present in minute traces.

The function of 'mineral' matters in food is to build up the main substance of the animal skeleton and to provide the material necessary for forming the saline constituents and inorganic acids of the blood, gastric juice, and other fluids and secretions of the body, as well as to supply elements, such as phosphorus, sulphur and iron, which form integral parts of the blood corpuscles and of muscular and other tissues.

The general composition of the various feeding stuffs in common use is stated in the accompanying tables. The items given are moisture (*i.e.* loss on drying at 100°C.), oil (ether extract), albuminoids, digestible carbohydrates, fibre and mineral matter (ash). The term 'digestible' as applied to carbohydrates here merely means rendered soluble during the process of successive boiling in weak mineral acid and weak alkali (for details see *Methods of analysis, infra*). The question of actual digestibility by the animal will be considered further on. The term 'albuminoids,' except where otherwise specified, means total nitrogen multiplied by 6·25, as is conventional for the purpose of commercial analysis. It has been already pointed out that the whole of the nitrogen in foods is not present in the proteid form, some portion being in the form of amides or similar bodies, but that in what are generally called 'concentrated' foods, such as seeds and seed products, the proportion of non-albuminoid nitrogen is relatively small, and not worth differentiation for the ordinary practical purposes of comparison of one sample with another. For instance, in barley, oats, maize, wheat, and rye, the actual albuminoid nitrogen is from 90 to 96 p.c. of the total nitrogen; in cotton cake, linseed cake, and ground-nut cake, and in brewers' grains, about 96 p.c.; in peas and beans, about 90 p.c.; in rice meal (rice bran), about 92 p.c.; and in wheat bran, about 86 p.c. In straw (a ripened stem, it may be noted), the proportion is about 90 p.c. In meadow hay it is less, namely, about 87 p.c. In young or immature

grass or clover, the proportion is only from about 70 to 75 p.c., and in grass or clover preserved in the moist state as silage it may be only 50 to 60 p.c., owing to partial degradation of the albuminoids by fermentation. In roots, the proportion of albuminoid to total nitrogen may fall below 40 p.c. (as in mangolds). In turnips, carrots, and potatoes, it is from about 50 to 60 p.c., and in cabbages probably about 70 p.c.

Before referring to the tabulated statement of composition of various foods, the reader should bear in mind that the analyses given are in most cases typical only of the average composition of each, and that considerable differences occur between different samples, which is, indeed, the reason why many of them are ordinarily subjected to analysis for the purposes of commercial transactions. These variations are often considerable even in natural grains such as oats, but are especially notable in the case of what may be called 'manufactured' feeding stuffs such as oil cakes. The feeding value of these is largely affected by the extent to which the oil has been pressed from the seed. Thus linseed cake, if lightly pressed, may contain 15 or 16 p.c. of oil. Under medium pressure, it may contain 12 p.c., and would still be regarded as rich in oil. Very commonly it is pressed down to 10 p.c., while very heavily pressed cake has often only 7 or 8 p.c. of oil, and sometimes, though rarely, as little as 5 or 6 p.c. Sometimes (or often in the case of cotton cake) the cake is ground and sold as meal. In such cases, it is especially important to have regard to the oil, as oil is largely extracted from some seeds, not by pressure, but by exhausting the finely ground seed with a volatile solvent such as petroleum spirit, in which case it may have only 1 p.c. of oil. This process is largely applied to rape seed and to soya beans. Again, in the case of linseed or rape cake, the percentage of albuminoids varies largely with the variety of seed from which the cake is made. Linseed cake, made from East Indian linseed, may contain from about 25 to about 30 p.c. of albuminoids; cake from Russian linseed, about 27 to about 35 p.c.; whilst cake made from American Western linseed sometimes contains nearly 40 p.c. of albuminoids. The composition of undecorticated cotton-seed cake varies according to whether it is made from the large smooth Egyptian seed or from the small thick-shelled and cotton-coated Indian variety. In the case of decorticated cotton-seed cake—made from American woolly seed stripped of its husk or 'hull'—the quality of the cake or meal depends largely upon the perfection with which the shelling process has been carried out. Often the separated shells are ground and partially put back after the decorticated seed has been crushed in the mills and the cakes reground to meal. Some foods are residual portions of grains, the main part of which is used for human food—as, for example, wheat-bran, rice meal (really rice-bran), and numerous foods made from various fractions of the maize kernel. These are necessarily of variable composition, according to the method and degree of separation from the other parts of the grain.

Owing to the importance of albuminoids in feeding, and to their special value for milch cows, and for balancing the natural poverty in albuminoids of natural fodders such as roots, 'concentrated' food stuffs are sometimes graded according to their richness in albuminoids. Thus, decorticated cotton cake or meal, groundnut (*Arachis*) cake, and soya-bean cake or meal, may be described as very rich in albuminoids (40 to 50 p.c.); linseed cake and rape cake as rich (say 25 to 35 p.c.); undecorticated cotton cake, beans, peas, and dried brewers' grains as moderately rich (20 to 25 p.c.); whilst wheat, oats, rye, barley, maize, feeding flour, rice meal, bran, pollards, and millet, would be described as relatively poor in albuminoids (10 to 18 p.c.).

In the case of fodder crops, such as grass and hay, the composition varies much with the stage of growth at which they are cut, as well as with the species of plants which constitute them.

The relative manurial value of the excreta yielded by the consumption of feeding stuffs depends largely on the proportion of nitrogen they contain, and to a minor extent on the phosphoric acid and potash contained in their ash. This aspect of their value is too complex to be entered upon here. A very full discussion of this part of the subject by Voelcker and Hall in the light of modern investigation, especially with regard to the question of compensation for unexhausted manurial value under the Agricultural Holdings Act, will be found in the Journal of the Royal Agricultural Society for 1902, 111.

Digestibility of feeding stuffs. It never happens in practice that an animal digests the whole even of the potentially digestible matters in its food. The quantity digested depends not only on the inherent potential digestibility of the food, but also on the species, age, condition, and individual constitution of the animal, and the quantity and quality of the food supplied to it. A large number of experiments have, however, been carried out, chiefly in Germany and in America, to ascertain as nearly as is practicable the proportion of the various kinds of nutritive matter actually digested in most of the feeding stuffs in use on the farm, the experiments having been made with the various farm animals, ruminant and non-ruminant. The composition of the food supplied to the animal is ascertained by analysis and its quantity weighed. The fæces are collected, weighed, and analysed, and the difference gives the quantity of each constituent digested. The experiments are carried on for a sufficient length of time to eliminate as far as possible errors due to previous feeding, the results for the first few days being neglected. The results, especially in the case of poor and bulky foods, are vitiated to some extent by such of the secretions of the alimentary canal as are voided with the excreta; while the results obtained with concentrated foods are complicated, and probably vitiated by the fact that such foods, in the case of ruminants, must necessarily be mixed with large quantities of bulky fibrous fodder, any variations in the digestion of which, brought about by the different conditions of feeding, become credited to the account of the concentrated food, which cannot be tried by itself. Despite these and other sources of inexactness, the study of the results of a number of experiments gives the nearest approach we can get to a faithful

AVERAGE OR TYPICAL COMPOSITION OF CONCENTRATED FEEDING STUFFS.

—	Moisture	Oil or fat	Albuminoids (=total nitrogen ×6·25)	Digestible carbohydrates[1]	Fibre	Mineral matter (ash)	Sand or silicious matter in ash
Cotton cake, decorticated	9·0	11·5	44·0	23·0	5·5	7·0	—
Do., do., undecorticated, from Egyptian seed	13·5	6·5	22·5	33·0	19·0	5·5	0·4
Do., do., from Bombay seed	12·0	4·5	19·0	35·5	22·0	7·0	1·5
Soya-bean cake	12·5	7·0	42·0	28·5	4·5	5·5	0·5
Earth-nut (arachis) cake, decorticated	9·0	10·0	51·0	21·3	3·5	5·2	1·3
Do., do., undecorticated	8·7	8·2	32·0	24·6	21·5	5·0	1·5
Linseed-cake	11·5	11·0	28·0	34·5	8·5	6·5	1·0
Sunflower-seed cake	7·0	10·0	30·5	24·5	21·0	7·0	1·0
Poppy-seed cake	10·5	8·5	38·5	20·5	9·0	13·0	1·3
Rape cake	10·5	10·0	33·0	29·8	9·0	7·7	2·0
Sesamé cake	9·0	12·0	39·0	23·0	5·0	12·0	2·0
Beans, English	14·0	1·5	25·5	49·5	6·5	3·0	—
Peas, do.	14·0	1·7	22·5	53·3	5·5	3·0	—
Cocoanut (copra) cake	9·0	10·0	21·0	42·5	12·0	5·5	0·3
Palm kernel cake or meal (pressed —not solvent-extracted)	10·0	9·0	16·0	41·2	20·0	3·8	—
Do., do., solvent-extracted	10·0	1·8	17·4	45·0	21·7	4·1	—
Dried brewers' grains	10·0	7·0	20·0	42·5	16·0	4·5	—
Wet do. do.	76·0	1·8	5·3	11·4	4·3	1·2	—
Wheat bran	13·0	4·0	14·0	55·5	8·0	5·5	—
Do. pollards	13·0	5·0	16·0	57·0	5·0	4·0	—
Do. middlings	12·0	4·0	16·0	61·0	4·0	3·0	—
Wheat	13·5	1·9	12·0	68·9	1·9	1·8	—
Oats	13·5	4·5	11·5	58·5	9·0	3·0	—
Rye	13·4	1·7	11·5	69·5	1·9	2·0	—
Barley	14·3	2·5	11·0	65·2	4·5	2·5	—
Maize	13·0	4·5	10·0	69·6	1·5	1·4	—
Rice meal or rice bran, Rangoon	8·5	15·5	12·5	48·7	6·0	8·8	1·8
Do., do., English	10·0	10·0	11·5	54·0	6·5	8·0	2·4

AVERAGE OR TYPICAL COMPOSITION OF MOIST OR BULKY FARM FODDERS.[2]

—	Moisture	Oil or fat	Nitrogenous substance		Digestible carbohydrates[1]	Fibre	Mineral matter (ash)
			Albuminoid	Non-albuminoid			
Pasture grass	76·7	0·9	2·9	1·1	10·9	5·2	2·3
Clover (about to flower)	81·0	0·7	2·6	0·8	8·1	5·2	1·6
Meadow hay, rich	15·0	2·3	10·2	1·8	39·5	24·0	7·2
„ „ medium	15·0	2·2	8·0	1·2	42·0	25·4	6·2
„ „ poor	14·0	2·0	6·3	0·5	41·1	31·0	5·1
Clover hay, medium	16·0	2·5	10·5	2·5	37·2	25·0	6·3
Oat straw	14·5	2·0	4·0		37·0	36·8	5·7
Wheat straw	13·6	1·3	3·3		39·4	37·1	5·3
Barley straw	14·2	1·5	3·5		39·1	36·0	5·7
Bean straw	18·4	1·1	8·1		31·0	36·0	5·4
Pea straw	13·6	1·6	9·0		33·7	35·5	6·6
Maize, silage	79·1	0·8	1·0	0·7	11·0	6·0	1·4
Mangolds, large	89·0	0·1	0·4	0·8	7·7	1·0	1·0
„ small	87·0	0·1	0·4	0·6	10·2	0·8	0·9
Swedes	89·3	0·2	0·7	0·7	7·2	1·1	0·8
Turnips	91·5	0·2	0·5	0·5	5·7	0·9	0·7
Potatoes	75·0	0·2	1·2	0·9	21·0	0·7	1·0
Field cabbages	85·7	0·7	1·7	0·8	7·1	2·4	1·6
Carrots	87·0	0·2	0·7	0·5	9·3	1·3	1·0

[1] By 'digestible' is here meant dissolved by successive boiling in acid and alkali (*see Methods of analysis, infra*)

[2] Compiled chiefly from averages calculated and tabulated by R. Warington.

estimate of what proportions of albuminoids or of fat or of carbohydrates will *probably* be digested and utilised in the average circumstances of farm feeding, and much credit is due to such investigators as Kuhn, Wolff, Kellner, Zuntz, Armsby, and others for their long and patient labours in this field of work, in which the pursuit of truth is impeded by so many pitfalls and obstacles. Ruminants have a better power of digestion than horses, especially for fibrous foods, and in this respect horses are better digesters than pigs. The following figures, extracted from a table compiled by Kellner, show the average results obtained with ruminant animals as regards the quantity of albuminoids, fat, 'soluble' carbohydrates, and fibre, out of 100 parts of each of these constituents, when supplied in the form of the more common feeding stuffs. By 'soluble' carbohydrates are here meant those dissolved by successive boiling with dilute acid and dilute alkali, usually termed in commercial analyses 'digestible.' As the latter word would here be ambiguous, the alternative term 'soluble' is used. (In German works this item of 'soluble' carbohydrates is usually rendered as 'nitrogen-free extract.') It will be noticed that with some foods, the experiments have been too few, having regard to the difficulty of such work, to lend any very strong validity to the figures. In other cases, the number of trials engenders more confidence in the probable general truth of the average figures, but it will be seen even in these cases that the range from minimum to maximum quantities digested in the experiments averaged is sometimes wide.

AVERAGE RESULTS OF FEEDING EXPERIMENTS ON FARM ANIMALS.

Matters digested out of 100 *parts of each constituent when supplied in the feeding stuff specified in the first column (from Kellner).*

—		Fat	Nitrogenous substance	'Soluble' carbohydrates	Fibre	Number of investigations
Cotton cake, decorticated	Range	93–100	84–96	44–71	0–100	14
	Average	94	86	67	28	
Cotton cake, undecorticated	Range	86–100	72–77	46–60	2–24	10
	Average	93	77	52	18	
Soya beans	Range	86–94	87–91	62–76	0–71	4
	Average	90	89	69	36	
Earth-nut (arachis) cake	Range	86–97	69–98	69–98	0–32	7
	Average	90	84	84	9	
Linseed cake	Range	86–97	80–90	60–96	0–92	14
	Average	92	86	78	32	
Sunflower-seed cake	Average	88	90	71	30	4
Poppy-seed cake	Average	92	79	64	61	3
Rape cake	Range	60–94	65–92	66–85	0–34	7
	Average	79	81	76	8	
Beans	Range	56–100	77–100	82–100	0–99	30
	Average	83	87	91	58	
Peas	Range	55–75	83–90	93–94	26–66	4
	Average	65	86	93	46	
Sesamé cake	Average	90	90	56	31	4
Cocoanut (copra) cake	Range	96–100	75–84	80–86	54–73	5
	Average	97	78	83	63	
Palm-kernel meal	Range	94–100	72–77	75–79	25–54	3
	Average	98	75	77	39	
Dried brewers' grains	Range	81–93	63–78	51–67	19–77	19
	Average	88	71	60	48	
Wet „ „	Range	84–89	71–74	56–74	33–45	12
	Average	86	73	62	40	
Wheat bran	Range	51–100	51–100	40–88	0–58	71
	Average	71	79	71	26	
Oats	Range	63–100	67–94	65–94	2–47	45
	Average	80	76	76	28	
Barley	Range	78–100	63–77	87–96	—	4
	Average	89	70	92	—	
Maize	Range	81–99	58–84	87–100	46–100	23
	Average	89	72	95	58	
Rice meal or rice bran	Range	82–87	48–65	67–92	0–51	14
	Average	85	57	80	15	
Pasture grass (April—May)	Range	63–68	71–79	75–84	70–75	4
	Average	66	75	79	73	
Meadow grass (June)	Average	62	70	75	66	2
„ „ (October)	Average	46	56	61	62	4
Meadow hay, rich	Range	45–68	60–73	58–76	53–80	48
	Average	57	65	68	63	

AVERAGE RESULTS OF FEEDING EXPERIMENTS ON FARM ANIMALS—*continued.*

		Fat	Nitrogenous substance	'Soluble' carbohydrates.	Fibre.	Number of investigations
Meadow hay, medium	Range	—	49–67	53–73	50–71	104
	Average	51	57	64	59	
„ „ poor	Range	—	35–61	49–65	46–64	34
	Average	49	50	59	55	
Clover hay, best	Range	44–74	56–71	63–76	38–54	19
	Average	63	65	70	49	
„ „ medium	Range	33–63	48–59	57–69	38–52	46
	Average	53	54	64	46	
Oat straw	Range	14–51	12–50	33–55	42–66	11
	Average	36	33	46	54	
Wheat straw	Range	17–44	0–26	29–40	42–59	10
	Average	31	4	37	50	
Barley straw	Range	35–43	17–27	38–57	53–58	7
	Average	39	25	53	54	
Bean straw	Range	49–60	45–54	64–73	34–53	5
	Average	57	49	68	43	
Pea straw	Average	46	60	64	52	2
Green maize plant	Average	72	65	73	67	16
„ „ „ as silage	Range	65–90	22–67	55–77	56–83	25
	Average	80	51	67	71	
Mangolds	Range	?	44–89	91–100	0–43	22
	Average		70	95	37	
Swedes	Average	93	62	99	?	2
Turnips	Range	?	57–90	88–97	0–100	10
	Average		73	92	51	
Potatoes	Range	?	23–88	82–99	?	30
	Average		51	90		
Cabbages	Average	84	80	95	74	2

Energy equivalents of feeding stuffs. The ultimate physiological value of any food constituent is largely dependent upon the quantity of potential energy producible by its oxidation in the system, or by the oxidation of the equivalent body substance that it replaces. This energy may be manifest in maintaining the heat of the body, or in the mechanical work effected in the various movements of the body, including locomotion, the pulsation of the heart and circulation of the blood, and the mechanism of respiration. Not a little of the energy latent in coarse fodder is expended in the mere work of mastication and the other mechanism of digestion. The excess of digested food over that portion spent in maintaining the temperature and effecting the movements incidental to quiescent existence, is stored up as body increase (as in a fattening ox) or used in the production of the fœtus or of milk (as in the case of a cow). In the case of a working animal, such as a horse, the excess of food digested is spent in the production of external mechanical work, such as traction; and so, of course, with a ploughing ox. The ultimate potential energy of a food-stuff is measurable by the heat generated by its complete combustion in oxygen, now usually determined for experimental purposes by burning a weighed quantity of the material with compressed oxygen in a steel bomb immersed in a known weight of water, and measuring the rise of temperature imparted to the water. Expressing the results of such determinations in large calories (a large calorie being the heat necessary to raise 1 litre of water 1 degree centigrade), the combustion of 1 gram of each of the following food constituents is found to give approximately heat as under:—

Oil or fat	9·4
Proteins	5·8
Starch or cellulose	4·1
Cane sugar	4·0
Dextrose or glucose	3·8
Milk sugar	3·9
Asparagine	3·4

In the consumption of feeding stuffs by animals, only a portion of the theoretical potential energy, as indicated by their combustion heat, is realised. In the first place, as we have already seen, only a fractional part of the food is digested, and only the digestible part can yield energy. Furthermore, the oxidation of the digested matter is incomplete. The oxidation of completely utilised proteins goes no farther than the production of urea, and, although the great bulk of the carbon of utilised food is exhaled in the completely oxidised form of carbonic acid, a portion is also given off in the unoxidised form of hydrocarbon gas or methane. In order to ascertain the energy either actually realised or potentially stored by the animal from a given diet, it is necessary to feed it in a respiration chamber fitted with such appliances that the fæces and urine can be separately collected, and the whole of the gases expired during the experiment collected and analysed. The heat or combustion equivalent of the food consumed is determined on accurately sampled portions of the daily diet. A similar determination in the dried fæces gives, by deduction, the potential heat energy in the food actually digested. A

combustion of the dried residue of the urine voided and a measurement of the carbonic acid and water produced by combustion of the dried unoxidised gases exhaled from the lungs and otherwise, give the data for deducting the fuel energy corresponding to these factors, and so the real or potential energy generated or stored in the animal is determined.

In order to trace the disposition of this energy, it is necessary, in addition to the foregoing determinations, to weigh accurately the water as well as the dry food consumed, and to determine accurately all moisture given off by by the animal in fæces, urine, breath, and perspiration, and also the carbonic acid evolved. By means of delicately constructed respiration calorimetric chambers, it is possible to make very exact determinations of the actual heat produced in or by the animal during the experiment, and from the whole of the data obtainable to calculate, not only what fraction of the total proteids, fat, and carbohydrates has been digested, but how much of them has been stored up in the form of flesh or fat, and how much is expended in what may be called maintenance energy and heat production. Some foods, such as hay, and especially straw, require so much energy for their mastication and digestion that only a relatively small portion of the actually digested matter may be available for increase of tissue or fat formation, or for the production (in a horse) of external work, a comparatively large quantity of heat being produced. In concentrated, easily digestible foods, the loss of energy between administration of the food and storage as flesh or fat is much less. Thus, Kellner has shown that, in the case of a fattening ox, only 41 p.c. of the potential energy in a pound of digested starch is lost or used in converting that which corresponds to the remainder into fat or other tissue. In the digested portion of meadow hay, the loss of energy involved in digestion and assimilation was over 58 p.c.; in that of oat straw, 62·4 p.c.; and in that of wheat straw, as much as 82 p.c. Similarly, Zuntz found in the case of the horse that only from 10 to 15 p.c. of available energy was consumed in the processes of digestion and assimilation in the case of maize, beans, and oats, the remainder being available for the performance of external mechanical work, while in the case of hay, the mere process of digestion and assimilation of the digestible portion consumed from 50 to 60 p.c. of the potential energy of such portion, leaving only from 40 to 50 p.c. available for 'work.' In the case of straw, the energy expended by the horse in mastication and digestion was found to be even greater than the whole of the potential energy in the portion digested, showing, apparently, that straw has a negative food value for horses, except as a 'filler' and diluent for more concentrated food.

Albuminoid ratio. By this term is meant the ratio of digestible protein or albuminoids to the digestible fat and digestible carbohydrates in the food. In order to state this on a uniform basis, fat is converted into its approximate equivalent in digestible carbohydrates by multiplying the fat by the factor 2·3, on the assumption that on the average the energy and fat-producing value of the latter is approximately 2·3 times that of the former. Thus, if a food contains 20 p.c. of digestible albuminoids, 10 p.c. of digestible fat, and 40 p.c. of digestible carbohydrates, the albuminoid ratio would be $20:(10\times2{\cdot}3+40)$, or 20 : 63, or approximately 1 : 3. Linseed cake has an albuminoid ratio of about 1 : 2, which is called a 'narrow' ratio; and maize of about 1 : 10, which is called a 'wide' ratio; while in mangolds the ratio is exceedingly wide, namely, about 1 : 85. The efficacy of a mixed diet for a specific purpose is much affected by its albuminoid ratio. Fattening or working animals get on well with a diet of a fairly wide ratio, such as from 1 : 8 to 1 : 10, though even in the case of fattening animals, the ratio should be narrower (1 : 5 or 1 : 6) in the early stages of feeding. Young growing animals, animals with young, and cows in milk, need a diet of correspondingly 'narrow' ratio, *i.e.* richer in proteids, such as 1 : 5.

The subject of the maintenance value, energy value, and productive value of the various feeding stuffs cannot be further pursued here. It may be advantageously studied in very thorough detail in The Principles of Animal Nutrition, by H. P. Armsby, of the Pennsylvania State Agricultural Experiment Station (English publishers, Chapman & Hall, Ltd., 1903). Readers may also be referred to Chemistry of the Farm, by R. Warington (Vinton & Co., Ltd., London, 1902); to The Feeding of Crops and Stock, by A. D. Hall (John Murray, London, 1911); and to Goodwin's English translation of The Scientific Feeding of Animals, by O. Kellner (Duckworth & Co., London, 1909). The last-named book contains very full tables showing the composition, digestibility, and energy values of most of the foods in use on the farm, and ration tables for the dieting of farm animals, compiled from the results of scientific investigation. A useful table, compiled by A. Smetham, showing the composition of a large range of feeding stuffs met with in commerce, including many materials not commonly offered as such to farmers, but in extensive use for the manufacture of compound foods, may be found in a paper reprinted from the Journal of the Royal Lancashire Agricultural Society for 1909, and published by Mawdsley & Son, of Liverpool, under the title of Some New Feeding Stuffs and their Relative Value as Cattle Foods.

Analysis of feeding stuffs. The following methods are those commonly in use :—

Moisture.—A weighed quantity (usually about 3 grams) of the material, finely crushed or powdered by passing through a small mill, is dried at 100°C. until it ceases to lose weight. The loss is taken to be moisture.

Oil.—This is usually determined by extraction with ethyl ether. The method officially laid down (1908) for use under the Fertilisers and Feeding Stuffs Act in England, is as follows :—

'A weighed quantity of the sample shall be placed in a Soxhlet thimble, which shall then be placed in the Soxhlet extraction tube and extracted with washed, redistilled ether. At the end of 3 to 4 hours, the thimble shall be removed from the Soxhlet tube, dried, and its contents finely ground in a small mortar previously rinsed with ether. The substance shall then be returned to the thimble, the mortar being washed out with ether, and the extraction continued for another hour.

'After evaporation of the solvent, the oil shall be dried at 100° and weighed. The oil shall be redissolved in ether, and any undissolved matter shall be weighed and deducted.

'In the case of samples containing saccharine matter, *e.g.* sugar meals, the weighed portion in the Soxhlet thimble shall be washed twice with water, and then dried, previous to the extraction.'

A convenient quantity to work upon for determination of oil is about 3 grams.

Albuminoids.—The percentage of albuminoids, as already stated, is, for the purpose of ordinary feeding stuff analyses, conventionally arrived at by determining the nitrogen and multiplying the percentage thereof by 6·25. Nitrogen is now almost universally determined by some modification of the Kjeldahl process. The details of the method, as officially laid down (1908) for use under the Fertilisers and Feeding Stuffs Act in England, are as follows:—

'A weighed portion of the sample shall be transferred to a Kjeldahl digestion flask; 10 grams of potassium sulphate and 25 c.c. of concentrated sulphuric acid shall be added, and the flask heated until a clear liquid, colourless or of light-straw colour is obtained. The operation may be accelerated by the addition of a small crystal of copper sulphate or a globule of mercury to the liquid in the digestion flask.

'The quantity of ammonia shall be determined by distillation into standard acid after liberation with alkali, and, where mercury has been used, with the addition also of sodium or potassium sulphide solution.

'The materials used shall be examined as to their freedom from nitrogen by means of a control experiment carried out under similar conditions with the same quantities of the reagents which have been employed in the actual analysis, one gram of pure sugar being used in place of the weighed portion of the sample. The quantity of standard acid used in this control experiment shall be deducted from the total quantity of acid found to have been neutralised in the distillation of the sample.'

A convenient quantity to work upon for the nitrogen determination will, in most cases, be found to be from 1 to 1·5 grams.

The percentage of 'true albuminoids' or proteid substances, as distinguished from non-proteid bodies such as amides, &c., is sometimes determined by what is known as the phenol method, but more commonly now by the copper oxide method.

The phenol method depends upon the coagulability of proteids by phenol. A quantity of from 1 to 2 grams of the powdered feeding stuffs is covered with a warm 4 p.c. aqueous solution of phenol, to which have been added a few drops of a freshly made aqueous solution of metaphosphoric acid. After 15 minutes, a little boiling phenol solution is added, and the mixture stirred and allowed to cool. The whole is then poured on to a small filter, which is washed with more of the same liquid, but cold. After drying, the filter and its contents are transferred to a Kjeldahl digestion flask, and the nitrogen is determined as already described (Church and Kinch).

The copper oxide method depends upon the power of moist copper hydroxide to unite with proteid substances to form insoluble compounds. The preparation of cupric hydroxide used is known as Stutzer's reagent. It is made by dissolving 100 grams of copper sulphate in 5 litres of water with the addition of 2·5 c.c. of glycerol. A dilute solution of sodium hydroxide is added until the liquid is just alkaline. The precipitate of cupric hydroxide is filtered off, drained, transferred to a dish, and washed by decantation with water containing 5 c.c. of glycerol per litre, until the washings are no longer alkaline. The precipitate is mixed in a mortar with water containing 10 p.c. of glycerol, and transferred to a stoppered bottle. A gelatinous mixture is thus obtained which, when shaken up, can be removed by means of a pipette. The determination of albuminoid nitrogen is made as follows: About 1 gram of the feeding stuff is weighed out, mixed with 100 c.c. of water and boiled or heated in the water-bath for 10 minutes. A quantity of the cupric hydroxide paste, containing about 0·8 gram of actual cupric hydroxide, is added, and the whole thoroughly stirred, warmed for a short time, and allowed to cool. When cold it is filtered and washed with cold water. After drying, the filter and its contents are transferred to a Kjeldahl digestion flask, and the nitrogen determined as above described. Instead of adding the cupric hydroxide paste directly to the solution, it is desirable to place the requisite quantity in a separate beaker, treating it with cold water, allowing it to settle, and pouring off the water in order to eliminate the glycerol, which is used merely as a vehicle for the preservation of the reagent.

Fibre.—A weighed quantity (conveniently about 3 grams) of the ground sample, either with or without previous extraction with ether, is boiled for half an hour with 125 c.c. of a 2 p.c. solution of sulphuric acid, the loss of water due to boiling being continuously made up. The fluid is diluted with a few hundred cubic centimetres of water, and allowed to stand for some time. The bulk of the fluid is then filtered off, any matter that becomes transferred to the filter being washed back again into the original vessel. The residue is then boiled with 125 c.c. of a 2 p.c. solution of potassium hydroxide, diluted, and filtered—this time through counterpoised filters. The fibrous matter is washed on to the filter, washed with boiling water until the washings are no longer alkaline, then with a little dilute acid, and then with water until the washings are no longer acid. It is next washed several times with methylated spirit, and, if the oil was not removed prior to the fibre determination, it must be finally washed several times with ether. Finally the fibre is dried to constancy in a water-oven, and weighed.

Ash.—A quantity of the material (for example, 3 grams) is placed in a platinum capsule and heated over an argand burner turned down low. The heating is continued over a yellow flame until the residue is free from carbon. The residue under incineration should be stirred from time to time with a platinum wire, being meantime lightly covered with an arched piece of platinum foil. Ignition over a Bunsen burner is more rapid, but is liable to result in loss of potash.

Sand and other silicious matter.—The ash,

after being weighed, is digested in the platinum basin with a little dilute hydrochloric acid, and the silicious matter filtered off, ignited, and weighed. This consists of sand, together with —in the case of some foods—silica derived from naturally silicious tissues, such as rice husks.

'*Digestible*' *carbohydrates.*—This item, which includes starch, sugars, mucilaginous matter, pentosan derivatives, and other bodies—sometimes also termed 'soluble carbohydrates' or, as in Germany, 'nitrogen-free extract'—is taken by difference. For the methods of determining the various sugars, starch, &c., separately, the reader is referred to other sections of this work. B. D.

FEHLING'S SOLUTION. It has long been known that a mixture of verdigris, honey, and vinegar, when boiled together to form an ointment, changes in colour from green to red.

Vogel (Schweigger's Journ. 13, 162) proved that the precipitate formed consisted of cuprous oxide, and later Buchner attempted to explain the part played by the sugar in the change. Trommer first used alkaline copper sulphate solution as a qualitative reagent for sugars, and succeeded in detecting one part of grape sugar in a million parts of water, and also in differentiating between different kinds of sugars (Annalen, 1841, 39, 360).

Alkaline copper solution was first applied to volumetric analysis by Barreswil (J. Pharm. Chim. 1844, [3] 6, 301), who added potassium tartrate to the solution, and the method of titration was worked out by H. Fehling (Annalen, 1849, 72, 106; 1858, 106, 75).

Various formulæ have been suggested for the preparation of Fehling's solution by Bödekerr Soxhlet, Meissl, Herzfeld, Allihn, Kjeldahl, &c. (Bruhns, Zeitsch. anal. Chem. 1899, 38, 78), but that recommended by Soxhlet is usually preferred, partly on account of its small alkali content.

34·64 grams of pure crystallised copper sulphate, powdered and dried by pressure between filter paper, is dissolved in distilled water and diluted to 500 c.c.; and 70 grams sodium hydroxide (of not less than 97 p.c.) and 180 grams of potassium sodium tartrate (Rochelle salt) are dissolved in 400 c.c. of distilled water and diluted to 500 c.c. Equal volumes of the two solutions are mixed to form the test, which should be kept in a carefully closed bottle to prevent absorption of carbon dioxide, and should not be unduly exposed to light. As the solution is liable to decomposition, a small portion should always be heated to boiling before commencing the test, and the liquid should not be used if any precipitation occurs. It is, however, preferable to keep the two solutions separate until shortly before use (Zeitsch. anal. Chem. 1890, 29, 615).

The Rochelle salt used is best prepared by dissolving commercial cream of tartar in hot water, rendering the liquid slightly alkaline after boiling by addition of sodium carbonate, filtering off the precipitated calcium carbonate, and crystallising the Rochelle salt from the filtrate.

Addition of small quantities of mineral acids to Fehling's solution by lessening its alkalinity effects its reduction, even when it is still alkaline to litmus. Often the action commences before the liquid is warmed, reduction being completed by gentle heating. The reduction is attributed to the decomposing action of the mineral acid upon the tartaric acid (Jovitschitsch, Ber. 1897, 2431). Evidence of the negative character of the blue ion in Fehling's solution was first adduced by Kahlenberg (Zeitsch. physikal. Chem. 1895, 17, 586), and later by Küster (Zeitsch. Elektrochem. 1897, 105) and Masson (Phil. Trans. 1899, 192, 331).

Masson employed a solution as free as possible from alkali, and electrolysed it in conjunction with a solution of copper sulphate, the blue ions in the two solutions travelling in opposite directions along a tube containing a jelly solution of potassium chloride. The presence of an invisible ion, probably tartaric ion, accompanying the negative blue ions, was demonstrated by the formation of a precipitate at the boundary of the positive blue ions, when the negative ions were still some way off.

The constituent salt of the neutral Fehling's solution was isolated and analysed by Masson and Steele (Chem. Soc. Trans. 1899, 75, 725), who represented its formation from cupric tartrate thus:

$$5NaOH+4CuC_4H_4O_6 = Na_2C_4H_4O_6+Na_3C_{12}H_7Cu_4O_{18}+5H_2O.$$

They also obtained evidence that the excess of alkali in Fehling's solution, as usually made, is combined with the blue salt.

F. Bulluheimer and E. Seitz (Ber. 1899, 2347; 1900, 817) showed that three classes of cupric tartrates exist; monotartrates, containing carboxylic and hydroxylic hydrogen, all replaced by metal; double salts consisting of monotartrate, probably united through copper to a molecule of basic alkali tartrates; and a third class consisting of monotartrate combined with basic cupric tartrate.

The salts in Fehling's solution, from their general reactions, appear to belong to the second class, and compounds having the formulæ $C_8H_4O_{12}CuNa_2K_2$ and $C_8H_4O_{12}CuNa_3K$ have been isolated.

The neutral cuprotartrate of Masson (*l.c.*) requires the addition of alkali in order to form the usual Fehling's solution with its characteristic colour.

Fehling's solution is *not reduced* by cane sugar, dextrin, or cellulose, but *is reduced* by dextrose, lævulose, maltose, lactose, mannose, galactose, arabinose, gallisin, aldehyde, chloral, chloroform, valeraldehyde, resorcinol, pyrogallol, gallotannic and trichloracetic acids, and by arsenious acid.

The action of these substances on the solution is doubtful. Among the products are formic, acetic, tartronic, and some acids of doubtful composition and a gum-like substance. Its use is almost restricted to the detection and estimation of reducing sugars. For the *detection* of sugars, the clear, acid-free liquid is heated with two volumes of Fehling's solution. If one of the above reducing compounds be present, a yellow precipitate of the hydrated cuprous oxide, which rapidly becomes converted into the orange-red anhydrous oxide, is produced.

If the liquid to be tested is much coloured, it must be first clarified, as described under SACCHARIMETRY. When the clarification has been

performed with lead, an amount of the solution containing a known weight (2 to 5 grams) of glucose or other body, estimated, is placed in a 100 c.c. flask and is treated with sulphurous acid gas, or with a strong solution of that gas, until the whole of the lead is precipitated, and, after the addition of a little freshly precipitated, washed alumina, is diluted to 100 c.c., agitated and filtered.

Cane sugar, when estimated, is first clarified, if necessary, and then 'inverted'—*i.e.* converted into a mixture of dextrose and lævulose. For this purpose, a solution containing not more than 1 gram of sugar to 4 c.c. of solution is mixed with one-tenth its bulk of fuming hydrochloric acid, and is heated to 70° for 10 to 15 minutes, and finally neutralised by addition of sodium carbonate.

Starch and starchy bodies may also be converted into invert sugar, and estimated by Fehling's solution. Two or three strong flasks, each containing from one-half to one gram of the substance and 50 or 60 c.c. of decinormal sulphuric acid solution, are closed with caoutchouc corks carefully tied down, and are heated in a water-bath. After 4 hours, one flask is taken out and contents neutralised and titrated with Fehling's solution as hereafter described, and after a further interval of 2 hours the second is similarly examined. If the amount of sugar found in the second flask does not exceed that in the first, the result may be taken as correct; but if the quantities differ markedly, the third flask is heated a further period of from 2 to 4 hours, and then titrated. Each 100 parts of invert sugar found represents 90 parts of starch.

In titrating solutions of any of these substances, 10 c.c. of Fehling's solution is carefully measured into a wide test-tube and diluted to about 40 c.c., and heated to boiling. The neutralised sugar solution, which should contain from one-half to one gram per 100 c.c., is then run in from a burette in portions of 2 c.c., the mixture being heated to boiling after each addition until the blue colour has nearly disappeared. The sugar is then added more cautiously until the supernatant liquid is colourless or slightly yellow. A few drops of the solution may be filtered and tested for copper by addition of sulphuretted hydrogen or of a mixture of potassium ferrocyanide and acetic acid.

The solution may be standardised for invert sugar in the following way: 4·75 grams of pure sucrose are dissolved in 75 c.c. of water and 5 c.c. of hydrochloric acid (sp.gr. 1·188) is added. The solution is then warmed to 70°, and maintained at that temperature for about 7 minutes, making a total of 10 minutes' heating. After inversion, the acid is exactly neutralised with sodium hydroxide, and the liquid diluted to 1 litre. 10 c.c. of this solution contains 0·050 gram of invert sugar, and should reduce 10 c.c. of the copper solution (*see also* Börntrager, Zeitsch. angew. Chem. 1893, 600).

Experience has shown that the time occupied during the analysis, the amount of excess of copper present at any moment in the solution, the concentration of the liquid, and other slight details, seriously affect the result. Soxhlet (Pharm. J. [3] 1880–1, 11, 721) has examined this question, and recommends close adherence to the following process, where extreme delicacy is required. Having approximately found the strength of the solution by running the sugar solution into 50 c.c. of Fehling's solution as above until the blue colour disappears, dilute it until containing about 1 gram per 100 c.c., and heat 50 c.c. Fehling's solution with as much of the diluted solution as should precipitate all the copper. When the sugar estimated is invert sugar, grape sugar, or lævulose, the heating should occupy 2 minutes, while for maltose and lactose 4 and 6 minutes respectively should be allowed. The whole fluid is then filtered and tested for copper. A third titration is next performed with a larger amount of the fluid, with 1 c.c. less of sugar (according to the presence or absence of copper), and the titrations are repeated with varying amounts of sugar solution, each time adding the whole of that solution at once, until 1 c.c. more or less would give a filtrate free from or containing a trace of copper, after which the variation in the amount of sugar solution is decreased. In this way, the volume of sugar solution required may be determined to 0·1 c.c. Under these conditions, 100 c.c. of the mixed copper reagent require 0·475 gram anhydrous dextrose or 0·494 gram of invert sugar for complete reduction. The following may be taken as the weight of sugar capable of reducing 10 c.c. of Fehling's solution:—

	gram
Dextrose, lævulose, or invert sugar	0·0500
Cane sugar (inverted) . . .	0·0475
Milk sugar (lactose) . . .	0·0678
Malt sugar (maltose) . . .	0·0807

Soxhlet (*l.c.*), operating by his method as described above, has obtained the following results. (His method of 'inverting' cane sugar has been somewhat objected to)—

WEIGHT OF SUGAR REDUCING 10 C.C. OF FEHLING'S SOLUTION.

—	Time of heating (mins.)	Undiluted	Diluted with			
			One vol. of water	Two vols. of water	Three vols. of water	Four vols. of water
Dextrose	2	0·0475	0·04825	0·0488	0·0492	0·0494
Invert sugar	2	0·0494	0·05030	0·0509	0·0514	0·0515
Lævulose	2	0·0513	0·05235	0·0530	0·0536	0·0526
Lactose	6	0·0676	Unaffected by dilution			0·0676
Lacto-glucose	2	0·0511	,,		,,	0·0533
Maltose	3 to 4	0·0778	,,		,,	0·0740

The titration of raw sugars and other coloured commercial products is very unsatisfactory when potassium ferrocyanide is used as an indicator, mainly because the amino compounds present cause the solution of much cuprous oxide, which then gives a precipitate with potassium ferrocyanide. On this account, indicators have been proposed which will show the presence of a trace of cupric salt without previous filtration, the best of these being ferrous thiocyanate (A. R. Ling, T. Rendle, and G. C. Jones, Analyst, 1905, 30, 182; 1908, 33, 160–170), which gives the characteristic red colour of ferric thiocyanate when treated with cupric salt solution. The reagent is prepared by dissolving 1 gram of ferrous ammonium

sulphate and 1·5 grams of ammonium thiocyanate in 10 c.c. of warm water, adding 2·5 c.c. of conc. hydrochloric acid, and completely removing all trace of ferric salt by addition of zinc-dust. The titration of the sugar solution is carried out much as usual, except that it must be done as quickly as possible to avoid oxidation (Ling, J. Inst. Brewing, 1906, 12, No. 1).

A modification of Fehling's process, devised by Pavy, is based on the fact that precipitation of the cuprous oxide is prevented by the presence of excess of ammonia, the solution losing its intense blue colour and becoming absolutely colourless after the whole of the copper has been reduced.

The solution used is prepared by mixing 120 c.c. of Fehling's solution with 300 c.c. of ammonia (0·880 sp.gr.) and 400 c.c. of 12 p.c. caustic soda solution, and diluting to 1 litre. 100 c.c. of this solution corresponds with 10 c.c. of Fehling's solution. The larger quantity of Fehling's solution (120 c.c. instead of 100 c.c.) used to prepare this test is required on account of the lower oxidising power of Pavy's solution, the action of which on invert sugar is only five-sixths of that of Fehling's solution. Its action on maltose and lactose also differs from that of Fehling's solution.

To prevent reoxidation of the decolourised solution, with reproduction of the blue colour, the operation should be performed without access of air, by connecting the burette supplying the sugar solution with a tube passing through a cork into the flask containing the Fehling's solution, the steam from which escapes through another tube dipping beneath the surface of mercury. A slow current of coal gas may be passed through the flask during the operation.

The sugar solution is run into the flask, in which 100 c.c. of the copper solution has been heated to ebullition, and the boiling is continued until the colour has disappeared. Hehner (Analyst, 1881, 6, 218) has shown that alkaline tartrates, carbonates, and other salts affect the results.

The method is most used in clinical chemistry, particularly for urine analysis. It is also of great value in studying the saccharine products of enzyme action, especially as it gives with glucose a very much larger 'copper' value than with maltose (Croft Hill, Chem. Soc. Trans. 1898, 73, 634).

The most accurate method of using Fehling's solution, especially when the sugar solution is unclarified, consists in separating and estimating the precipitated cuprous oxide. One of the many processes recommended is that of Pavy. The Fehling's solution is boiled, in slight excess, with the sugar solution, the strength of which should be about 1 p.c., and the precipitated suboxide is rapidly separated by filtering the liquid through a funnel loosely packed at the neck with glass wool or asbestos. The precipitate, after washing, is dissolved in hot dilute nitric acid, or 2 c.c. conc. nitric acid, or a mixture of dilute sulphuric and nitric acids, and the copper estimated by electro-deposition. The weight of copper obtained is multiplied by 0·5395 to obtain its equivalent in inverted cane sugar, or by other factors, which may be calculated from the tables given above, to obtain the equivalent of any other sugar which may be estimated.

Brunner recommends solution of the cuprous oxide, filtered as above, in a solution of pure ferric chloride or sulphate acidulated with sulphuric acid, and the estimation of the ferrous salt so produced, by titration with a standard solution of potassium permanganate or dichromate.

The cuprous oxide can also be weighed directly after washing with alcohol and ether. It may also be estimated as metallic copper after reduction by hydrogen or as cupric oxide after ignition in porcelain.

FELSPAR or Feldspar. (Ger. *Feldspat*; Fr. *Feldspath.*) A name applied to a group of silicates, of great importance as rock-forming minerals. The felspars may be classified according to their crystallographic symmetry, in two great series. One series crystallises in the monoclinic system, and since its members present two well-marked cleavage planes at right angles to each other, they are distinguished as *orthoclastic* felspars. The other series crystallises in the triclinic or anorthic system, and as these felspars have their principal directions of cleavage more or less inclined to each other, they are termed *plagioclastic*. The first series is represented by *orthoclase* or common potash-felspar ($KAlSi_3O_8$); while the plagioclastic group includes *albite* or soda-felspar, and *anorthite* or lime-felspar, with several intermediate species, such as oligoclase and labradorite, which contain both soda and lime. As the proportion of Ca increases, that of Na diminishes, and the felspar becomes more basic.

According to Tschermak, only two distinct species of plagioclase are to be recognised—viz. albite $NaAlSi_3O_8$, and anorthite $CaAl_2Si_2O_8$. The other felspars of this group may be regarded as isomorphous mixtures of these extreme types, as shown in the following scheme, where Ab represents the molecule of albite, and An that of anorthite :—

Albite	. .	Ab_1An_0 to	Ab_6An_1
Oligoclase	. .	Ab_6An_1 „	Ab_3An_1
Andesine	. .	Ab_3An_1 „	Ab_1An_1
Labradorite	. .	Ab_1An_1 „	Ab_1An_3
Bytownite	. .	Ab_1An_3 „	Ab_1An_6
Anorthite	. .	Ab_1An_6 „	Ab_0An_1

In addition to these, there are several other members of the felspar group, some of which, though of theoretical interest, are of little practical importance. In orthoclase, sodium may replace the potassium, and there may be a transition through soda-orthoclase to nearly pure $NaAlSi_3O_8$, for which the name *barbierite* has been proposed (W. T. Schaller, 1910). Dimorphous with this group of monoclinic felspars we have a triclinic group represented by *microcline* ($KAlSi_3O_8$), soda-microcline, and *anorthoclase* ($[Na,K]AlSi_3O_8$), which differ essentially only in their optical characters from the preceding. In the plagioclase series, a soda-anorthite ($Na_2Al_2Si_2O_8$) has been recognised and named *carnegieite* (H. S. Washington and F. E. Wright, 1910). Several barium felspars are also known.

As illustrations of the chemical composition of the chief felspars, the following analyses are selected :—

——	I	II	III	IV	V	VI
SiO_2	65·72	68·46	62·30	58·11	52·55	45·97
Al_2O_3	18·57	19·31	22·00	28·16	28·32	33·28
Fe_2O_3	—	0·28	0·04	—	2·44	1·12
K_2O	14·02	—	0·94	0·44	0·64	—
Na_2O	1·25	11·27	8·20	5·17	4·52	1·85
CaO	0·34	0·68	4·86	5·35	11·61	17·21
MgO	0·10	—	—	1·52	0·48	—
	100·00	100·00	98·34	98·75	100·56	99·43

I. Orthoclase, sp.gr. 2·55; from Baveno, by Abich. II. Albite, sp.gr. 2·61; from Arendal, by G. Rose. III. Oligoclase, sp.gr. 2·66; from Elba, by Damour. IV. Andesine, sp.gr. 2·64; from near Marmato, by Deville. V. Labradorite, sp.gr. 2·71; from Neurode, Silesia, by G. vom Rath. VI. Anorthite, sp.gr. 2·75; from Hecla, by Damour.

The specific determination of the felspars is often a matter of difficulty, without recourse to analysis; but much aid is afforded by a determination of the optical characters (extinction angles and interference-figures on cleavage flakes and in thin sections of rocks) and of the sp.gr. The latter is most conveniently taken by suspending fragments of the mineral in heavy liquids of known density. The following are the typical average values: orthoclase and microcline, 2·57; albite, 2·62; oligoclase, 2·64; andesine, 2·65; labradorite, 2·69; bytownite, 2·71; and anorthite, 2·75. To the chemist a more ready means of determination is afforded by Szabó's method, which consists in examining the flame-reactions produced on exposing a fragment of the mineral in a Bunsen flame, the colouration of the flame being compared with standard tables (Szabó, Ueber eine neue Methode die Feldspathe zu bestimmen, Budapest, 1876).

Without introducing mineralogical details of the numerous felspars, which would require a long article, it may be convenient to refer briefly to the principal varieties. *Orthoclase* occurs usually in white, grey, or flesh-coloured crystals, often twinned; the finest examples being obtained from the granite of Elba, Baveno, and Carlsbad. The clear translucent variety, known as *adularia*, is found chiefly in the Swiss Alps and in Ceylon. The orthoclastic felspar of volcanic rocks is termed *sanidine*, and occurs in tabular glassy crystals, which are especially fine in the trachyte of the Drachenfels on the Rhine.

Microcline is a felspar closely related to orthoclase, and formerly regarded as monoclinic, but shown by Des Cloizeaux to be triclinic. A green variety known as *amazon-stone* occurs in fine crystals in the Ilmen Mountains in the Urals, and at Pike's Peak in Colorado. The colour is lost on heating the mineral, and is therefore not due, as formerly supposed, to the presence of copper. An organic salt of iron has been suggested by König as the probable colouring matter in the Pike's Peak mineral.

Albite, the ordinary soda felspar, so called from its dead white colour, occurs chiefly in granites and diorites; fine crystals being found, with chlorite, in the rocks of Tyrol. *Pericline* and *cleavelandite* are names applied to varieties of albite. A mixture of albite and orthoclase or microcline, in red bands, occurs at Perth in Canada, and is hence known as *perthite*. *Oligoclase* is a soda-lime plagioclase, occurring in granite and gneiss, notably at Arendal in Norway and at Miask in the Urals; while it is found also in volcanic rocks, as at Vesuvius. *Andesine* is a somewhat rare felspar from the volcanic rocks of the Andes. *Labradorite* is an important mineral, brought originally from the coast of Labrador, where it constitutes with hypersthene the rock known as norite. Exhibiting in many cases a beautiful change of colour when viewed in different directions, it is valued as an ornamental stone; but most of the labradorite which occurs in gabbro, dolerite, basalt, and other basic rocks does not present this appearance. The *bytownite* of Thomson has been shown to be rather widely distributed as a constituent of certain eruptive rocks.

Anorthite is found in gabbro, porphyrite, andesite, and basalt; distinct crystals, though rare, occurring at Monzoni in Tyrol and at Monte Somma.

The chief use of felspar in the industrial arts is for the manufacture of porcelain. Orthoclase is employed partly as a constituent of the body in certain wares, but principally as a glaze, for which purpose large quantities are imported from Norway. Here the felspar is quarried from pegmatite-veins in Sætersdalen and along the coast between Bamle and Arendal; about 34,000 tons are exported annually. Other countries producing felspar in large quantities are Sweden, Bavaria, Ontario, and the eastern United States. (E. S. Bastin, Economic Geology of the Feldspar Deposits of the United States, Bull. U.S. Geol. Survey, 1910, 420.) The price ranges from 12*s.* to 15*s.* per ton. The discovery of a vein of red felspar at Belleek, in Co. Fermanagh, Ireland, led to the establishment of porcelain works at this locality. The red felspar becomes white on calcination, the iron passing into the condition of magnetite, the particles of which may be removed by means of a magnet.

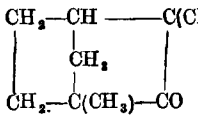
Felspars rich in alkalis have been sometimes used as manures. Very pure felspar finds a limited application in the manufacture of artificial teeth. Several varieties of felspar are cut and polished as ornamental stones, the most important being labradorite, which is used for table-tops, umbrella-handles, and various trivial objects. The mineral was first brought to this country in the 18th century, by the Moravian missionaries, from St. Paul's Island off the coast of Labrador. The schiller and colour of labradorite are partly due to microlitic enclosures and lamellæ of diallage. *Moonstone* is a variety of adularia from Ceylon, exhibiting a faint bluish opalescence, which has led to its employment in jewellery. *Sunstone* is a form of oligoclase, occurring at Tvedestrand in Norway, remarkable for its reddish sheen, due to enclosed lamellæ of specular iron-ore. Among other ornamental felspars may be mentioned the opalescent albite from Canada, known as *peristerite* (περιστερά, a pigeon) from the resemblance of its colours to those on the neck of a pigeon; and a variety of anorthoclase displaying a brilliantly coloured metallic reflection from the augite-syenite of Norway. L. J. S.

FENCHENE *v.* FENCHONE.

FENCHONE $C_{10}H_{16}O$. A ketone isomeric with camphor. It is optically active, *d*-, *l*-, and *r*- fenchone all being known. *d-Fenchone* was discovered by Wallach in fennel oil. The fraction boiling at 190°–195° is treated with

three parts of concentrated nitric acid to oxidise anethol and other impurities. The product is poured into water, the separated oil being washed with caustic soda solution, distilled in steam, dried, and finally crystallised at a low temperature (Wallach and Hartmann, Annalen, 259, 324; Wallach, *ibid.* 263, 129). *d*-Fenchone also occurs in small quantities in Russian oil of anise (Bourchardat and Tardy, Bull. Soc. chim. [iii.] 15, 616; Compt. rend. 1896, 122, 624).

Pure fenchone is a colourless oil, b.p. 192°–193°; sp.gr. 0·9465 at 19°; prolonged cooling at low temperatures causes it to solidify to large crystals, m.p. 5°–6°; μ_D=1·46306 at 19°, moleo. ref. =44·23; $[\alpha]_D$+71·97°. It is not oxidised in the cold by nitric or sulphuric acids, but potassium permanganate converts it into dimethylmalonic, oxalic, and acetic acids. By heating it for six days with concentrated nitric acid, there are formed dimethylcarballylic, dimethylmalonic, *iso*camphoronic, *iso*butyric, and acetic acids, together with a nitrofenchone (Gardner and Cockburn, Chem. Soc. Trans. 1898, 708; Semmler, Chem. Zeit. 1905, 29, 1213; *cf.* Konowaloff, J. Russ. Phys. Chem. Soc. 1903, 35, 953); and by heating with sulphuric acid at 80°, 4-aceto-1 : 2-xylene is formed (Marsh, Chem. Soc. Trans. 1899, 1058). Warming with phosphorus pentoxide yields *m*-cymene, b.p. 175°–176° (Wallach, Annalen, 275, 157). Reduction by sodium in amyl alcohol or treatment with phthalic anhydride yields *l-fenchyl* alcohol $C_{10}H_{17}OH$; m.p. 45°; b.p. 197°–200°; $[\alpha]_D$ −10·35° (Bertram and Halle, J. pr. Chem. [ii.] 61, 293). This is converted by phosphorus pentachloride into *fenchyl chloride*, b.p. 84°–86°, which, on heating with aniline, is converted into the terpene *fenchene* $C_{10}H_{16}$, b.p. 150°–152°. A solid fenchyl chloride, m.p. 92°, has been obtained by Kondakoff from fenchyl alcohol (J. pr. Chem. 1909, [ii.] 79, 271). Fenchene has been prepared synthetically by treating nopinone and bromacetic ester with zinc and hydrolysing the hydroxy ester thus formed (Wallach, Annalen, 363, 1). Fenchene is oxidised by concentrated nitric acid, yielding *cis*-camphopyric acid and its anhydride. Phosphorus pentachloride reacts with fenchone yielding chlorfenchenephosphinic acid $C_{10}H_{14}ClPO(OH)_2$, chlorfenchene and α- and β-chlorfenchene hydrochlorides (Gardner and Cockburn, Chem. Soc. Trans. 1897, 1157; 1898, 275, 704). Ammonium formate reacts with fenchone, yielding the formyl derivative of D.*l*-fenchylamine from which the free base $C_{10}H_{17}NH_2$ is easily obtained; b.p. 195°; sp.gr. 0·9095; $[\alpha]_D$−24·63°. Sodium nitrite and acetic acid react with fenchylamine, producing D.*l*-fenchene, an isomeric hydrocarbon, *d*-limonene and cineol (Wallach, Annalen, 362, 174). D.*l*-fenchene, when warmed with acetic and sulphuric acids, yields *iso*fenchyl alcohol, b.p. 201°–202°, which, on oxidation with chromic acid, yields *iso*fenchone $C_{10}H_{16}O$, b.p. 201°, sp.gr. 0·943 at 18·5°, $[\alpha]_D$+9° 35′. By heating fenchone and bromine in a sealed tube for 24 hours, bromfenchone, b.p. 131°–134° (18 mm.), is obtained. Alcoholic potash converts bromfenchone into γ-fencholenic acid, which on being dissolved in concentrated sulphuric acid and poured on to ice, yields an isomeric compound, m.p. 77°; three fencholenic acids are known (Wallach, Annalen, 315, 273; Chem. Zentr. 1899, ii. 1052; Czerny, Ber. 1900, 2287; Balbiano, Gazz. chim. ital. 1900, 30, ii. 382; Semmler and Bartell, Ber. 1906, 3960; 1907, 432). Like camphor, fenchone reacts with sodium, forming a pinacone $C_{20}H_{34}O_2$, b.p. 219° (13 mm.), m.p. 97°. The constitution of fenchone is still under discussion, but the evidence available seems to indicate the following formula:—



(Wallach, Annalen, 369, 63; Semmler, Ber. 1907, 4591; Bouveault and Levallois, Compt. rend. 1908, 146, 180; *cf.* Glover, Chem. Soc. Trans. 1908, 1285).

l-Fenchone was discovered by Wallach in thuja oil. The fraction boiling at 190°–200° may be warmed with nitric acid to oxidise the thujone and then steam distilled or better be oxidised with potassium permanganate to destroy the thujone and then treated with semicarbazide hydrochloride, which reacts with the *l*-camphor, which is also present more quickly than with the *l*-fenchone, and forms an effective agent for separating them (Wallach, J. Pharm. Chim. 1896, 3, [9] 465; Chem. Zentr. 1905, ii. 675; Annalen, 353, 209). *l*-Fenchone has b.p. 192°–194°, m.p. 5°, $[\alpha]_D$ − 66·94°, and forms a series of derivatives similar to those obtained from *d*-fenchone. For *r-fenchone* and its derivatives, *v.* Bouveault and Levallois, Compt. rend. 1909, 148, 1399, 1524.

For further references to fenchone and derivatives, *v.* Wallach, Annalen. 284, 324; 300, 294; Semmler, Ber. 1906, 2577; Mahla, Ber. 1901, 3777; Rimini, Gazz. chim. ital. 1909, 39, ii. 196; Bouveault and Levallois, Bull. Soc, chim. 1910, [iv.] 963, 968 (*v.* KETONES).

FENUGREEK. *Trigonella Fœnum græcum.* A plant possessing a characteristic flavour, used largely as a condiment for cattle.

According to analyses by D'Ancona (Landw. Versuchs-Stat. 1899, 51, 387), the dry matter contains—

Protein	Fat	N-free extract	Crude fibre	Ash
13·4	3·4	47·0	30·6	5·6

The pure ash contained—

K_2O	Na_2O	CaO	MgO	Fe_2O_3	P_2O_5	SO_3	SiO_2	Cl
19·1	7·6	29·8	1·0	4·9	8·1	4·1	23·5	1·1

In composition, fenugreek resembles crimson clover and it is recommended as a farm crop. Since, however, the peculiar flavour of the plant is transmitted to both milk and meat, the fodder is more suited for working animals than for fattening or milk production. The peculiar odour and flavour of the plant is said to be due to an oil; it is very pronounced in the spring, but becomes less when the plant ripens.

The seeds contain trigonelline $C_7H_7NO_2$, the betaine of pyridine- 2-carboxylic acid (Jahns, 1885). Among the carbohydrates in the seeds of fenugreek is a mannogalactan, which, under the influence of a soluble ferment, produced on germination, hydrolyses with the formation of

reducing sugars (Bourquelot and Herissey, Compt. rend. 1900, 130, 42, and 731). H. I.

FERGUSONITE. A rare mineral consisting of columbate (and tantalate) of yttrium and cerium earths together with a small amount of uranium, the general formula being $R'''(Cb,Ta)O_4$. Tetragonal crystals were found in Greenland in 1826, but usually the mineral is massive with a lustrous, pitchy appearance on the fractured surfaces; sp.gr. 5·8. It is optically isotropic, owing to alteration and hydration: when heated, it suddenly shows an incandescent glow, becomes fractured and anisotropic, and gives off gases (helium, &c.). The mineral occurs in pegmatite-veins at Ytterby in Sweden, near Arendal and elsewhere in Norway, and in some abundance as large masses at Barringer Hill in Llano Co., Texas. At the last-named locality, it has been mined, together with gadolinite (*q.v.*) and other rare-earth minerals, for the supply of yttrium, &c. L. J. S.

FERMENTATION (including Enzyme Action and Chemical Action of Bacteria).

History of the development of ideas about fermentation. The phenomena of alcoholic fermentation seem to have been familiar to man from the earliest times in the processes of the production of wine, accompanied by effervescence and frothing, and of the baking of bread, accompanied by the rising of the dough. These obvious characteristics of fermentation find expression in the names applied in various languages both to the process itself (fermentation, Lat. *fervere*, to boil; *Gährung*, from a Teutonic root, *jesen*, to froth, from which the word *yeast* is also derived) and to the agent by which it was caused (yeast, as above, leaven, *levure*, from the Lat. *levare*, to raise; *Hefe*, Ger. *heben*, to lift; referring to the rising of the scum of yeast in fermentation and the rising of the dough in baking).

The term *fermentation* was at first applied without distinction to all changes accompanied by effervescence, but after 1659 (Sylvius de la Boë) gradually became limited to alcoholic fermentation, along with such cases of acid fermentation and putrefaction as were accompanied by evolution of gas.

Further knowledge of the chemical nature of fermentation came from the experiments of Lavoisier (1789), who showed that in alcoholic fermentation, the sugar was quantitatively decomposed into alcohol and carbon dioxide (together with some acetic acid). These relations were rendered more precise by Gay-Lussac (1810), whose conclusions may be summed up in the equation of alcoholic fermentation:

$$C_6H_{12}O_6 = 2CO_2 + 2C_2H_6O.$$

Fermentation was looked upon as a chemical process set up by an unknown agent, termed the ferment, produced by the oxygen of the air from the fruit juices, &c., which underwent the change, this view being founded on the observation (Gay-Lussac) that boiled grape juice only fermented after exposure to air. The process of fermentation had been regarded by Willis (1659) and Stahl (1697) as consisting in a violent internal motion of the particles of the fermenting substance set up by an aqueous liquid, a conception which was replaced by that of catalytic force by Berzelius (1839), according to which the ferment, like other catalytic agents, was found unchanged at the end of the process. Liebig (1839), on the other hand, held the view that the ferment was an unstable body which itself underwent decomposition and that it was the internal motion due to this which was transferred to the fermentable substance and brought about its decomposition. The action only persisted as long as this metamorphosis of the ferment was in progress, and came to an end when this ceased. The ferment itself was regarded, in agreement with Gay-Lussac, as being formed by the action of oxygen on the nitrogenous materials of the fermentable liquid, and the amount produced was dependent on the special nature of this, and might be, as in brewing, more than sufficient to cause the decomposition of the whole of the sugar present.

These views were founded on the belief that yeast was a chemical substance comparable to any of the well-known organic products. Even before the publication of the views of Berzelius and Liebig, however, strong evidence had been brought forward that this was not the case. As early as 1680, Leeuwenhoek had described the granular appearance of yeast under the microscope and 'animalcules' of putrefying materials had also been observed; but in spite of a few other isolated observations, it was not until about 1836 that the intervention of living organisms in fermentation and putrefaction was rendered probable. In that year, Schulze showed that infusions of various animal and vegetable materials remained free from all putrefaction, if, after they had been well boiled, they were only allowed to come in contact with air which had passed through sulphuric acid The same thing was subsequently shown by Schwann to hold if the admitted air were heated, and the observations were extended to alcoholic fermentation. The conclusion was drawn by both these investigators that putrefaction was caused by living germs present in the air, which developed in the putrescible liquid. The microscopic examination of a fermenting sugar solution revealed the presence of yeast cells capable of reproduction by budding, and Schwann attributed to this living organism, which he named 'Zuckerpilz' (sugar fungus), the production of alcoholic fermentation. Curiously enough, almost simultaneously with Schwann, two other investigators, Cagniard-Latour in France and Kützing in Germany, came independently to the same conclusion, as the result of microscopic observations. These conclusions were rejected by Berzelius and Liebig, who replied to them by the theories already mentioned, but, in spite of this powerful opposition, they gradually won for themselves a considerable body of adherents, especially in Germany and among those engaged in brewing (*see* Hefe, Fäulniss und Gährung, 208–229, Berlin, 1904).

The evidence in favour of this vitalistic view of the cause of fermentation was greatly strengthened by the experiments of Schröder and von Dusch (1864), who discovered the important fact, which has proved to be an almost indispensable feature of bacteriological technique, that air lost its power of producing putrefaction when it was simply filtered through cotton wool. Many difficulties, however, still remained unexplained,

which prevented the universal acceptance of the vitalistic view. Milk, for example, was found to become sour after having been boiled, in spite of all precautions, and no organism could be recognised in it capable of producing the change. Moreover, other ferments existed, such as diastase (Dubrunfant, 1830; Payen and Persoz, 1833), which, like yeast, lost their power of action when heated, and yet were completely soluble in water and devoid of all trace of organisation.

The final proof that fermentative changes in general, such as the alcoholic and lactic fermentations, putrefaction, &c., were actually produced by living organisms was afforded by the classical researches of Pasteur (Compt. rend. 1857, 45, 913). Pasteur showed, in the clearest possible manner, that every fermentation was produced by a specific organism. He regarded fermentation as indissolubly bound up with the life of the organism, and summed up his conclusions in the aphorism, 'No fermentation without life.' The recognition of micro-organisms as the cause of fermentation rendered it necessary to differentiate between these so-called organised ferments and the substances, such as diastase, invertase, pepsin, &c., which had gradually become known, and which could be extracted from the higher plants and animals and even from micro-organisms, and were therefore known at first as soluble ferments, and later, following the suggestion of Kühne, as *enzymes* (ἔν, in; ζύμη, yeast).

A long discussion then arose on the question whether any essential difference existed between the modes of chemical action of these two classes of ferments. Moritz Traube (1858) formulated the theory that all chemical action of micro-organisms was due to enzymes produced in the cell of the organism, and he was supported by Berthelot, Hoppe-Seyler, and many others. Pasteur, on the other hand, maintained his original thesis, and, stimulated by his discovery (Compt. rend. 1861, 52, 344, 1260) that many micro-organisms could live in the absence of free oxygen, developed the view that fermentation was life without free oxygen, the physiological function of the process being to supply the organism with the oxygen or the energy necessary for its metabolism. Pasteur's theories, aided by his brilliant exposition and ingenious experiments, gained the day for the vitalistic view, especially as the supporters of Traube's conception were unable, in spite of many attempts, to adduce positive evidence of the isolation of an enzyme capable of producing one of the fermentations characteristic of living organisms. A middle path was taken by Nägeli, who suggested the idea that the power of producing fermentation was restricted to the living protoplasm of the cell, and consisted in the transference of a molecular vibration from this to the fermentable substance.

This theory was disproved and the original idea of M. Traube strikingly confirmed in 1897 by Eduard Buchner, who succeeded in preparing from yeast a liquid capable of fermenting sugar. It has since been shown that the lactic and acetic fermentations can also be produced in the absence of living cells. Buchner's experiments disprove the vitalistic theory as held by Pasteur, and the view is now generally adopted that micro-organisms produce chemical change by means of enzymes present in their cells. The chemical changes produced by micro-organisms are thus brought into line with those effected by the numerous and well-known enzymes secreted by the cells of various organs of the higher plants and animals as well as by micro-organisms, and the modern conception of fermentation embraces all the different changes produced by these various agents.

General properties of enzymes. It has been found that enzymes bring about chemical change by acting as catalytic agents; that is to say, they greatly increase the velocity of the particular reaction in question without themselves undergoing any permanent change. No very definite criterion of an enzyme as distinguished from a catalyst in general, exists, but the term is generally limited to catalysts formed by living organisms, and it is an almost invariable rule that enzymes in solution are thermolabile, losing their activity as a rule rapidly at 70°. In the absence of moisture, on the other hand, they are much more stable, and may be heated in some cases to 110° for a considerable time without being destroyed. In this respect, the inactivation of enzymes by heat bears a close resemblance to the heat coagulation of proteins (Chick and Martin, J. Physiol. 1910, 40, 404).

Chemically, the enzymes are presumably of a very complex character, but they have, up to the present, evaded the skill of the chemist, no one of them having been isolated in a pure condition and submitted to investigation. It appears, however, to have been established with some degree of probability that certain enzymes (pepsin, diastase) are not proteins. All enzymes appear to form colloidal solutions, and in agreement with this they only possess very slight powers of diffusion, so that they only pass slowly and imperfectly through the ordinary dialysing membranes.

Ecto- and Endo-enzymes. In many cases, the enzymes, after being elaborated in the cell, are excreted into the surrounding medium, in which they produce their characteristic effects. This is the case, for example, with some of the digestive ferments of the animal body, the ptyalin of the salivary gland, the pepsin of the stomach, the trypsin of the pancreas (in this case in an inactive form) being all poured into some portion or other of the alimentary canal. In other cases, the enzyme does not pass out of the cell, the chemical change in question taking place inside the cell. The best known case of this kind is probably that of alcoholic fermentation, which occurs entirely inside the yeast cell.

A second point of difference lies in the behaviour of enzymes towards solvents. Many enzymes (*ectoenzymes*) can readily be extracted by such solvents as water, normal saline (0·8 p.c. sodium chloride solution), and glycerol from the cells after the organism has died. Thus pepsin and chymase, the enzyme of rennet, can be extracted by weak acid or glycerol from the membrane of the stomach of the calf or other animal. Again, invertase and maltase, which only pass out of the living yeast cell in very small amount, can be removed by water from dried and heated yeast. Others again cannot be removed from the cell in this way until the cell wall has been

ruptured, and these are termed *endoenzymes* or *intracellular enzymes*. The autoclastic enzymes of the animal body are instances of this, as are also the zymase and tryptase of yeast. (It has, however, been shown that zymase can be extracted from dry yeast by simple maceration with water: Lebedew, Compt. rend. 1911, 152, 49.)

Extraction of enzymes. These facts provide the clue to the practical methods adopted for the extraction of enzymes.

1. *Soluble enzymes* can be extracted by digesting the finely divided material which contains them with water, saline, or glycerol. The enzyme solution is then poured off, pressed out or separated by centrifugalisation, according to circumstances, and either used directly or submitted to some process of purification. In some cases it is necessary or advisable to treat the material with dilute acid to convert the inactive proenzyme or zymogen of the cell into the active enzyme. As in the instances of invertase and maltase mentioned above, it is essential that the cell shall be killed before being submitted to extraction. This is best accomplished in these cases by treatment with chloroform or ether (invertase) or by drying and heating the yeast (maltase).

2. *Insoluble or endo-enzymes* are extracted by first of all rupturing the cells by some process of grinding, and then removing the liquid cell contents by simple pressure with or without the addition of some substance like kieselguhr, which greatly facilitates the process, but has the disadvantage of retaining some of the enzyme. A typical instance of this is afforded by the preparation of yeast juice from yeast by the method of E. and H. Buchner and Hahn, which is described below under the heading of *Alcoholic fermentation*. In other cases, the tissue or organ may be simply minced or frozen and finely sliced, and may then be extracted with water or saline.

Dry preparations of enzymes. A solution of an enzyme in an aqueous fluid often loses its characteristic properties very quickly, either on account of the instability of the enzyme itself, or because of the presence of other enzymes which bring about its decomposition. Such solutions are, moreover, extremely liable to infection by moulds, yeasts, and bacteria, and must either be kept at a low temperature or treated with some antiseptic. Dry preparations are found to be much more permanent, and, when quite dry, can be kept for long periods without undergoing much loss of power.

They may be obtained, in the first place, by the evaporation of the solution *in vacuo* at as low a temperature as possible, the product being usually a scaly mass. A second and often more convenient method consists in precipitation by alcohol, nearly all enzymes being insoluble in 75–90 p.c. alcohol. The chief practical difficulty of this method lies in the fact that aqueous alcohol frequently appears to exert an extremely detrimental effect on the enzyme, so that the process must in such cases be carried out with great rapidity. The final dehydration is usually effected by treatment of the precipitate with absolute alcohol and then with ether, a fine white powder being thus obtained.

It is not, however, in all cases necessary to extract the enzyme from the organism which contains it. Thus, for example, crushed castor-oil seeds are commonly used for the purpose of decomposing fats by means of the lipase which they contain. Buchner and his colleagues have, moreover, been able to effect several types of fermentation (alcoholic, lactic, acetic) by means of the cells of the organism, which have been simply killed by dry heat or killed and dehydrated by treatment with alcohol and ether or with acetone.

Purification of enzymes. The preparations obtained by the foregoing methods are all extremely crude, and contain, in addition to other enzymes, large proportions of extraneous matter, chiefly consisting of mineral salts, especially phosphates, proteins, and carbohydrates. Many attempts have been made to remove these by various processes of chemical precipitation (lead acetate, &c.), salting out, dialysis, treatment with yeast to remove sugars, &c., and thus to arrive at a pure enzyme. Some of these cases are mentioned later on, and there is no doubt that a considerable degree of purification can be effected by these methods. The usual experience has, however, been that with increasing freedom from such substances, the enzyme becomes more and more susceptible of change, and finally loses its activity before anything which can be regarded as an individual chemical compound has been isolated.

Mode of action of enzymes. Enzymes act as catalysts, but differ from catalysts of known symmetrical constitution in being specific in their action. The three disaccharides, sucrose, maltose, and lactose, for example, are all hydrolysed by the same acids, whereas each of them requires for its enzymic hydrolysis a special enzyme, which has no action whatever on the other two. The most probable view as to the mode of action of enzymes upon the substance to be decomposed, known as the substrate or zymolyte, is that in the first place some sort of combination between the two occurs, and that this is then followed by the comparatively slow breaking up of this complex, with liberation of the enzyme and the products of decomposition of the zymolyte.

It would, therefore, be expected that as long as excess of enzyme were present, the reaction would follow the ordinary course of a catalytic change. As soon as a certain limit of concentration of the substrate is reached, however, there is sufficient of it to combine with the whole of the enzyme, and any further increase in its concentration is then unable to produce any increase in the number of decompositions per unit of time, or in other words, after a certain concentration is reached, equal amounts of the substrate will be decomposed in equal times. These conditions appear to be realised in most cases of enzyme action, but since the absolute concentration of the enzyme is usually very small, the second period of the reaction, decomposition of equal amounts in equal times, is usually the more obvious.

Most of the enzymic decompositions which have been studied from this point of view, are cases of hydrolysis, which, in the presence of acids alone follow the usual course for which the equation $K=1/t(\log a/a-x)$ holds. This same expression should therefore hold for the enzymic

reaction when excess of enzyme is present, and this is actually found to be the case. When, however, the relations of concentration are such that equal amounts are decomposed in equal times, K, calculated by the foregoing expression, would increase with the time instead of being constant. On the other hand, anything which lessens the effective concentration of the enzyme will lower the rate of action and lead to a decrease of K. In many enzyme actions, there are at least three causes which tend to produce this effect. In the first place, the enzyme itself tends to become inactive. This change sometimes proceeds too slowly to have any effect on the result (*e.g.* in Senter's experiments on the decomposition of hydrogen peroxide by hæmase); in other cases, it occurs so rapidly as to influence the velocity very perceptibly (*e.g.* in alcoholic fermentation by yeast juice, in which the fermentation ceases for this reason). In the second place, the products of the reaction often diminish the rate of change to a greater or less extent. Thirdly, a state of equilibrium is often attained short of complete decomposition, and this also causes a decrease in K. Very valuable information can be obtained about the course of the reaction by determining the *initial velocity* of the change under various conditions of concentration, as these inhibiting influences are thereby, to a large extent, eliminated. In this way, A. J. Brown showed that the apparent monomolecular course of the inversion of cane sugar by invertase was, in reality, due to secondary effects. When a series of concentrations of sugar were taken, the initial rates of change were found to be equal, whereas in presence of the products the rate of change diminished almost in agreement with the monomolecular law. This same effect is obvious in the results of Hudson with cane sugar, of Kastle and Loevenhart with the decomposition of ethyl butyrate by lipase, and of Euler with alcoholic fermentation by yeast juice.

It appears, therefore, that, as a rule, the velocity curve of an enzyme reaction expresses the resultant of a very complicated system of phenomena, and can only be properly interpreted when a considerable number of experiments have been made to ascertain all the factors concerned.

When the substrate is present in large excess, increase of concentration of the enzyme frequently increases the rate of change proportionally, in agreement with the usual experience with inorganic catalysts. This is, for example, true for invertase. In some cases, however, the rate increases in proportion to a fractional power of the amount of ferment. This is the case when pepsin acts on dissolved albumins, the amount of action in equal times being proportional to the square root of the amount of pepsin (Schütz), and this rule appears to hold for many enzyme actions. It is explained by Arrhenius on the ground that the enzyme combines, with the products of the reaction (Immunochemie, Leipzig, 1907). In other cases, the amount of action is found to be constant when the product of amount of ferment and time is constant, or $F \times t = k$. This holds for the action of pepsin on coagulated albumin, and for that of trypsin on caseinogen (Hedin), and in many other cases.

The inhibiting influence of the products of the reaction is in many cases specific, numerous instances of this having been observed among the sugars and amino-acids. Thus invertase is inhibited by fructose (A. J. Brown), but not by glucose (Armstrong); lactase by galactose but neither by fructose nor glucose, &c.

As regards the nature of the combination between enzyme and substrate, very little is known. Some authors, however, regard it as highly probable that it is of the nature of adsorption between the particles of the colloidal enzyme and the substrate, and find in this an explanation of such relations as are exemplified by the proportionality between amount of action and the square root of the amount of enzyme, discussed above (*see* Bayliss, The Nature of Enzyme Action, vii.).

Whatever the nature of the combination, it appears to render the enzyme less susceptible of change whether by rise of temperature, spontaneous decomposition, or the action of other enzymes.

Reversibility of enzyme action: synthetic action of enzymes. Since enzymes act as catalysts, it might be expected from analogy with catalysts of known composition that they would bring about conditions of equilibrium by affecting the velocities both of the reaction itself and of the reverse reaction (Tammann, Zeitsch. physiol. Chem. 1892, 16, 271). Thus it might be expected that an enzyme which effected the hydrolysis of a disaccharide into two hexose molecules would, when added to a mixture of these two hexoses in the proper concentration, synthesise the disaccharide. In each case the reaction would proceed until equilibrium was produced, and the same equilibrium would be attained whether the disaccharide or the mixed hexoses formed the starting-point.

This extremely important property of enzymes was first experimentally demonstrated by Croft Hill (Chem. Soc. Trans. 1898, 634) in the case of the action of maltase on maltose, and so many instances have since been observed that reversibility of action may now almost be taken as a general property of enzymes.

The simplest case, so far observed, is the action of lipase on esters of the fatty acids which exhibits all the characteristic features of a reversible reaction (Kastle and Loevenhart Amer. Chem. J. 1900, 24, 491). These observers found that the hydrolysis of ethyl butyrate by the lipase of the pancreas or liver of the pig was always incomplete, and that when this enzyme was added to a mixture of butyric acid and alcohol (N/30), about 5 p.c. of the butyric acid was converted into ethyl butyrate in 40 hours at 25°, no ester being formed in a control experiment with the boiled enzyme solution.

The reaction studied by Croft Hill deserves consideration as the first observed case of synthesis resulting from enzyme action. The change in question was subsequently found to be of great complexity, and unanimity of opinion on the question has not yet been attained. The essential facts observed by Hill were: (1) that when concentrated glucose solution was acted on by the maltase of yeast, a portion of the glucose was converted into a disaccharide of higher rotation and lower reducing power; (2) that when such a solution was diluted, the disaccharide was reconverted almost completely

into glucose. These observations were interpreted to mean that in concentrated solution, a certain proportion of maltose (15 p.c. of the glucose in a 45 p.c. solution) had been formed synthetically from the glucose, and that on dilution the condition of equilibrium had been shifted in the direction of almost complete decomposition of the maltose back again into glucose. It was, however, subsequently found by Emmerling (Ber. 1901, 34, 600), that the disaccharide formed consisted chiefly of a sugar isomeric with maltose, which was identified by Emmerling as the *iso*maltose obtained by Fischer by the action of acids on glucose, but was regarded by Croft Hill as a new sugar, revertose. E. F. Armstrong (Proc. Roy. Soc. B, 1905, 76, 592) has confirmed Emmerling's result as to the nature of the chief product formed, and has further obtained the paradoxical result that emulsin which decomposes *iso*maltose, but not maltose, converts glucose into maltose, and not, as might have been expected, into *iso*maltose. Each enzyme, therefore, according to Armstrong, produces from glucose the disaccharide which it is unable to hydrolyse.

This remarkable result has not yet been confirmed, and Armstrong did not ascertain whether the maltose formed by the action of emulsin was decomposed by the same enzyme preparation when its solution was diluted. Moreover, only a very small proportion of maltose appears to have been formed. The simplest explanation of Croft Hill's experiment seems, therefore, to be that adopted by Bayliss, that the maltase employed contained emulsin (which has since that time been shown by Henry and Auld (Proc. Roy. Soc. 1905, B, 76, 568) to be present in yeast), and that each enzyme synthesised from glucose the particular disaccharide which it was capable of decomposing (*see also* E. F. Armstrong, The Simple Carbohydrates and Glucosides, 75; Fajans, Zeitsch. physikal. Chem. 1910, 73, 25; 75, 232).

A suggestion has also been advanced that the synthesis and hydrolysis of the same compound are effected by different enzymes which occur together but are each only able to discharge the single function of hydrolysis or synthesis (*see* Rosenthaler, Biochem. Zeitsch. 1908, 14, 238; 1909, 17, 257). This idea is rendered improbable by the fact that in many cases the same state of equilibrium is attained when enzymes of different origin are employed.

It has, however, been pointed out by Fajans (*l.c.*) that the enzyme itself probably takes part in the equilibrium, and that therefore alteration in its concentration might affect the state of equilibrium. This fact would also explain the observation that the equilibrium in certain cases of decomposition of acid esters is not the same when attained by the use of enzyme as when brought about by acid. The synthetic action of enzymes is still a little-known branch of the subject, but is of enormous importance in the biological chemistry of the living organism, since it is probably by the aid of reactions of this kind that the whole work of building up the tissues is effected.

Asymmetric and selective action of enzymes It has been shown by the researches of Marckwald, McKenzie, and others (Ber. 1904, 37, 349, 1368, 4696; Chem. Soc. Trans. 1905, 1373; 1906, 688) that in a reaction in which an asymmetric carbon atom is produced, the two possible optically active isomerides may be produced in unequal quantities provided that the possibility is afforded by the introduction of an optically active radicle that the resulting compounds shall not be optical antipodes. Thus the reduction of pyroracemic acid

$$CH_3 \cdot CO \cdot COOH$$

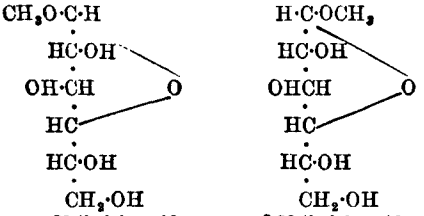
leads to the formation of inactive *dl*-lactic acid $CH_3 \cdot CH(OH) \cdot COOH$, whilst the reduction of menthyl-pyroracemate $CH_3 \cdot CO \cdot COOC_{10}H_{19}$ proceeds asymmetrically and yields an excess of the ester of the *l*-acid. More recently, it has been shown by Bredig and Fajans (Ber. 1908, 41, 752) that a catalytic reaction may proceed asymmetrically when the catalyst is itself optically active. This has been found to be the case when *l*-nicotine is employed to catalyse the decomposition of *dl*-camphorcarboxylic acid, the *d*-acid being in this case the more rapidly decomposed. This is precisely analogous to what occurs in many enzyme reactions, the asymmetric catalyst being in these cases the particular enzyme involved. There is, it is true, no direct positive evidence that enzymes are optically active substances, since, as already mentioned, no enzyme has as yet been isolated, but there is a strong probability that this is the case.

A good example of this asymmetric enzyme action is to be found in the work of Dakin (J. Physiol. 1904, 30, 253), who showed that the two optically active components of inactive *dl*-mandelic ester, which are hydrolysed at equal rates by alkalis, are decomposed at different rates by the fat-splitting enzyme or lipase of the liver, the dextro- ester being the more rapidly hydrolysed, so that after the removal of the resulting acid, the residual ester is lævorotatory. This action is probably to be explained by the formation of compounds between the enzyme and each of the components of *dl*-mandelic ester. The enzyme being, as explained above, itself an optically active substance, two different compounds are formed and these are decomposed at different rates. Many instances of this asymmetry of action are known among the chemical changes produced by micro-organisms. Thus the oxidation of inactive hydroxy acids (McKenzie and Harden, Chem. Soc. Trans. 1903, 83, 424), and of the amino acids by moulds, which was used by Pasteur for the resolution of such compounds, proceeds in a precisely similar manner; both of the components are attacked, but one more rapidly than the other. Similarly, the so-called alcoholic fermentation of the amino acids by yeast, as the result of which they are converted into carbon dioxide, ammonia, and an alcohol, takes place more rapidly with one of the components than with the other, so that by this means *l*-alanine and *d*-leucine can readily be prepared from the inactive synthetic acids (Ehrlich, Biochem. Zeitsch. 1906, 1, 8), the other component being, in each case, more easily decomposed.

An extreme case of this asymmetry of action is presented by many enzymes which only act on one stereoisomeride, and leave the other entirely untouched. Some remarkable instances of this kind have been revealed by the

researches of Fischer and his colleagues on the enzymes which bring about the hydrolysis of the disaccharides and the glucosides. The relations between enzyme and zymolyte, which exist in this group of compounds, have been likened by Fischer to those which exist between a lock and key. The enzyme is capable of combining with one stereoisomeride, but is of such a structure that not only does the change to the opposite optical isomeride prevent combination, but even a change in the arrangement of the groups which condition asymmetry round a single carbon atom in the molecule of the sugar, just as the change of a single ward of a lock prevents the key from fitting it. The classical example of this relation is afforded by the behaviour of maltase on the one hand, and emulsin on the other, to the various disaccharides and glucosides.

Glucose forms two stereoisomeric methyl esters, which only differ from one another in the arrangement of the groups round the terminal carbon atom, so that their configurations may be represented as follows :—



α-Methylglucoside. β-Methylglucoside.

One of these is arbitrarily known as α-methylglucoside, and the other as β-methylglucoside. Of these, the α- compound only is attacked by maltase and the β- compound only by emulsin, and precisely similar relations exist between the α- and β-ethyl glucosides. Hence maltase has received the more precise name of α-glucosidase (or sometimes α-glucase), whilst emulsin (or that constituent of the complex usually termed emulsin, which effects this particular change) is termed β-glucosidase. Neither of these enzymes will attack the β- and α-methyl glucosides of *l*-glucose, which are the exact optical antipodes or 'mirror images' of the α- and β-methyl *d*-glucosides, and moreover they also have no action on the corresponding derivatives of *d*-mannose, *d*-galactose, and *l*-xylose, although in each of these three cases the difference between the unattacked compound and the corresponding glucose derivative extends only to one carbon atom. On the other hand, β-methyl tetramethyl glucoside, in which four of the hydrogens of the hydroxyl- groups of β-methyl glucoside have been replaced by methyl is hydrolysed by emulsin, so that this extensive introduction of the methyl-group has less effect than a change in the symmetry of a single carbon atom.

The other enzymes capable of hydrolysing disaccharides are equally specific. Invertase, for example, hydrolyses cane sugar (and possibly raffinose, which, like cane sugar, contains the fructose group), but has no action on maltose, lactose, or the α- and β-methyl glucosides. Similarly, lactase only attacks lactose, and not cane sugar, &c.

The alcoholic enzyme of yeast also possesses a highly specific character, but is not affected by such small changes in configuration as are maltase and emulsin. Thus *d*-glucose, *d*-mannose, and *d*-fructose are all fermentable by yeast, whilst, on the other hand, *l*-glucose, *l*-mannose, and *l*-fructose are not fermentable, and this is also true of the pentoses.

Similar results have been obtained by Fischer and Abderhalden (Zeitsch. physiol. Chem. 1905, 46, 52) in examining the action of pancreatic juice on the synthetic polypeptides. Only one half of the racemic compound is attacked and the products of hydrolysis are always those active amino-acids which are contained in the natural proteins. Thus racemic alanylglycine

$$CH_3\cdot CH(NH_2)\cdot CO\cdot NH\cdot CH_2\cdot COOH$$

yielded glycine and *d*-alanine as hydrolysis products, *l*-alanylglycine being left untouched.

All these facts afford the strongest evidence that combination between enzyme and zymolyte precedes the decomposition of the latter, and there is little doubt that similar conditions hold generally for the synthetic action of enzymes, although but few instances of this have hitherto been studied. A striking case in point is the combination between hydrocyanic acid and benzaldehyde. Ordinarily these substances combine to form inactive benzaldehyde cyanhydrin $C_6H_5\cdot CH(OH)\cdot CN$. When, however, this reaction is carried out in the presence of emulsin (or rather of that constituent of emulsin which is distinguished as hydroxynitrilase), the resulting product is optically active, a greater proportion of the *d*- than of the *l*-cyanhydrin having been formed (Rosenthaler, Biochem. Zeitsch. 1908, 14, 238), and in one case the *d*- compound being the sole product.

In nature, the asymmetry of action of synthetic enzymes is of the most far-reaching importance, as is evidenced by such facts as that the sugars, proteins, and many other naturally occurring compounds, are all optically active. Moreover, the asymmetry of action is so great that in many cases, *e.g.* the sugars, the optical antipodes of the compounds appear not to occur at all.

Zymogens. The formation of enzymes in the cell is a subject of great importance, about which very little is known. In many cases, however, it has been ascertained that the cell contains an inactive substance, termed a zymogen or proferment, which subsequently becomes active and can often be rendered so by treatment with dilute acid. A very striking instance is afforded by the inactive trypsinogen of the pancreas. This substance is contained in pancreatic juice, and is quite inactive. When it is mixed with intestinal juice it is converted into active trypsin, by the action of a specific substance known as *enterokinase*, which is itself in all probability an enzyme. A case of even greater complexity is that of the enzyme thrombase, which brings about the clotting of blood.

Coenzymes. Some enzymes are incapable of producing their characteristic effects in the absence of a second substance, usually of a less complex character, which is therefore termed a coenzyme. The nature and functions of this class of substance are little understood (*see Alcoholic fermentation*).

Classification and nomenclature of enzymes. The nomenclature of enzymes is based on the principle that the name should indicate the substance acted upon by the enzyme, and should end with the syllable *-ase*, which is adopted as a specific termination, signifying an enzyme. This system introduces some difficulties, as certain compounds are decomposed in different ways by different enzymes (*e.g.* amygdalin and raffinose), and some enzymes decompose many different compounds (*e.g.* the digestive enzymes). These difficulties are avoided as far as possible by the use of special terms, such as emulsin, tryptase, invertase, lipase, and further specification is also sometimes attained by adding the names of the products formed.

Some confusion exists in actual practice, owing to the name, not of the substance decomposed, but of the product being prefixed to the termination -ase. Thus alcoholase is occasionally used for the alcohol-producing enzyme of yeast, but such terms should, as far as possible, be avoided, as well as those which simply denote the origin of the enzyme, such as hæmase (for the catalase of blood).

The simplest and most natural mode of classifying enzymes is by the nature of the reactions which they catalyse. Each group may then be further subdivided according to the nature of the compound upon which the specific action is exerted.

The chief enzymes at present known thus fall into the following groups, which agree in the main with those adopted by Oppenheimer, Euler, and other writers.

A. Enzymes producing hydrolysis (hydrolases).

1. Lipases, decomposing fats and esters; sometimes divided into:

(*a*) Esterases, decomposing simple esters.

(*b*) Lipases, decomposing fats and lipoid compounds, such as lecithin, &c.

2. Enzymes capable of converting aldehydes into an equimolecular mixture of acid and alcohol.

3. Enzymes hydrolysing the complex saccharides and glucosides (carbohydrases).

(*a*) Disaccharases, such as invertase, maltase, lactase, melibiase, &c.

(*b*) Tri- and tetra-saccharases, such as raffinase.

(*c*) Polysaccharases, such as diastase or amylase, inulase, cytase or cellulase, glycogenase, &c.

(*d*) Glucosidases, such as emulsin, rhamnase, &c.

4. The digestive enzymes, hydrolysing the proteins, polypeptides, amides, and analogous compounds. This is a very complex group, the precise relations of which are not at all understood, there being at present no available information as to the number of enzymes concerned in such a process as peptic or tryptic digestion. These enzymes are sometimes termed proteases and amidases.

(*a*) Simple amidases, causing the hydrolysis of various amino- compounds, such as urea, arginine, adenine, &c.

(*b*) Peptases and ereptases, decomposing polypeptides into amino-acids.

(*c*) Tryptases, comprising a large number of enzymes, occurring both in animal and vegetable organisms, which decompose proteins and carry on the decomposition to the amino- acid stage.

(*d*) Peptinases, comprising the enzymes of the animal stomach and of some plants, which in acid solution hydrolyse proteins, producing albumoses, peptone, and polypeptides.

B. Enzymes producing coagulation (coagulases).

1. Thrombase, which produces the clotting of blood.

2. Chymase, or rennet, which effects the curdling of milk.

3. Pectase, and similar enzymes.

C. Enzymes producing oxidation (oxidases and peroxidases).

1. Alcohol oxidases, oxidising alcohol into acetic acid.

2. Aldehydases, converting aldehydes into acids.

3. Purinoxidases, effecting the oxidation of the purin bases.

4. Phenolases, tyrosinases, &c., which effect the oxidation of many aromatic *p*-hydroxy and amino- derivatives.

D. Enzymes producing reduction (reductases).

E. Enzymes producing decompositions involving rupture of a carbon chain. These are sometimes known as zymases, or fermentation enzymes.

1. Enzymes of lactic acid fermentation.

2. Enzymes of alcoholic fermentation.

3. Many other enzymes doubtless fall into this group, since there is little doubt that the various fermentative changes brought about by bacteria, &c., are largely due to enzymes of this class. As, however, this has not yet been proved except in the foregoing cases, these cannot at present be enumerated here.

F. Enzymes producing the decomposition of hydrogen peroxide into water and oxygen (catalases).

Any attempt at a detailed account of the enzymes is impossible on account of limitations of space, and only the best investigated can be even briefly described.

Enzymes producing Hydrolysis.

Lipase. Enzymes capable of hydrolysing fats, lecithins, and the alcohol esters of the fatty acids occur both in the animal and vegetable kingdoms. Some authorities distinguish between the ester-decomposing enzymes, which they term esterases, and the true fat-splitting enzymes or lipases, but it is doubtful whether our knowledge of the subject is sufficient to justify this. The difficulty of discrimination between different enzymes in this group is greatly increased by the facts that not only do the enzymes themselves appear to be insoluble in water, but the fats are also insoluble. These circumstances render the determination of the rate of action extremely uncertain.

The lipases of the animal body occur practically in all the tissues, but the action of most of these appears to be confined to the decomposition of esters, such as ethyl butyrate (*see* Kastle and Loevenhart, Amer. Chem. J. 1900, 24, 491).

The chief fat-splitting enzymes of the body are found in the secretions of the pancreas and intestine. It seems probable that at all events the greater part of all absorbed fat is hydrolysed

before absorption, and this process takes place in the intestine. These enzymes are extremely sensitive to acids and oxidising agents; they decompose alcohol esters as well as fats. The filtered extract and the residue prepared from these insoluble enzymes are both inactive, whereas the mixture is active, and the inactive residue can be rendered active by the salts contained in bile (Magnus, Zeitsch. physiol. Chem. 1904, 42, 169; 1906, 48, 373; Rosenheim, J. Physiol. Proc. Feb. 19, 1910, 14). How far this phenomenon depends upon the solubility relations of the enzyme or the fat, is not known.

The vegetable lipases occur in the form of zymogen in the seeds, and become active during germination. The enzyme of castor-oil seed has been the most thoroughly investigated. Like animal lipase, it appears to be insoluble in water, but it differs from this in having very little action on the esters of the lower fatty acids (Armstrong, Proc. Roy. Soc. 1905, B, 76, 606). It is only effective in the presence of free acid and is rendered most effective by N/10 to N/3 sulphuric acid (Connstein, Hoyer, and Wartenstein, Ber. 1902, 35, 3988). Under these circumstances, it is so efficacious that it is employed technically for the hydrolysis of fats.

The synthetical action of animal lipase (or esterase) and its asymmetric decomposition of *dl*-esters have already been mentioned.

Invertase. Our knowledge of this enzyme, which brings about the hydrolysis of cane sugar to fructose and glucose, and owes its name to the inversion of the direction of rotation from dextro- to lævo-, which accompanies the change, is largely due to the classical researches of O'Sullivan and Tompson (Chem. Soc. Trans. 1890, 834). It occurs in many, but not all, species of yeast and in many moulds and bacteria, as well as in the higher plants and the intestine of animals. It is usually prepared from brewers' yeast; the enzyme can only be very imperfectly extracted from the living cells, especially when a young and vigorous culture is employed, but readily passes into solution in water when the yeast has been dried and heated or treated with chloroform, toluene, or alcohol. It is also present in the yeast-juice obtained by Buchner's grinding process, but is best prepared by allowing the pressed yeast to stand in a flask until it has become liquid, precipitating with 47 p.c. alcohol, and grinding the precipitate with absolute alcohol. Two kilos. of yeast thus yield 5 grams of a grey powder containing about 3·5 p.c. of nitrogen and 5–8 p.c. of ash. The activity is usually expressed as the time taken for a solution of 0·05 gram of the material dissolved in 5 c.c. of 0·5 normal sodium dihydrogen phosphate to reduce the rotation of 20 c.c. of 20 p.c. cane sugar solution to zero at 20°, and for the preparation obtained as above, this is about 25 minutes. More active preparations can be obtained by redissolving in 25 parts of water, treating with 2·5 parts of animal charcoal for an hour, shaking with 10 parts of kaolin, and reprecipitating with alcohol. This process yields a material containing only 0·36 p.c. of nitrogen and 2·07 p.c. of ash, and having an activity of 14 minutes, this being the most active preparation so far described (Euler, Lindberg, and Melander, Zeitsch. physiol. Chem. 1910, 69, 152). This result, combined with earlier observations of Osborne (*ibid.* 1899, 28, 399) and Salkowski (*ibid.* 1901, 31, 306) render it improbable that invertase is a protein, but the question is by no means settled. In *Monilia candida* (Bon.), invertase occurs as a true endo-enzyme which can only be obtained from the cell by rupture of the membrane (Fischer and Lindner, Ber. 1895, 28, 3034; Buchner and Meisenheimer, Zeitsch. physiol. Chem. 40, 167). The action on cane sugar is accelerated by acids up to a certain concentration, the optimum concentration of hydrogen ions being $10^{-4\cdot4}$ to $10^{-4\cdot6}$ (Sörensen, Compt. rend. Carlsberg, 1909, 8, 1), and is at once inhibited by alkalis. The glucose is liberated in the α- form, so that the rotation falls when an alkali is added, and considerable errors may be introduced in estimations of the rate of action by polarimetric observations from this cause (O'Sullivan and Tompson; Hudson, J. Amer. Chem. Soc. 1908, 30, 1160). According to Visser (Zeitsch. physikal. Chem. 1905, 52, 257), equilibrium is attained in normal cane sugar solution in presence of invertase when 99 p.c. has been hydrolysed and a corresponding synthesis (1 p.c.) probably occurs in a solution of fructose and glucose, although this has not been directly proved.

Solutions of invertase hydrolyse raffinose, a trisaccharide yielding fructose, glucose, and galactose on complete hydrolysis, but it is not certain whether this is actually due to the invertase or whether a specific raffinase is present. Certain organisms appear to hydrolyse cane sugar but not raffinose (*Mycoderma*) and others to hydrolyse raffinose but not cane sugar (*Schyzosaccharomyces octosporus* (Bey.)). (For the use of invertase in the estimation of cane sugar, *see* J. Soc. Chem. Ind. 1911.)

Maltase is best obtained from well-washed bottom fermentation yeast by drying it *in vacuo*, powdering, heating gradually to 100°, and then digesting for 3 days at air temperature with 10 parts of 0·1 p.c. caustic soda solution and toluene, and finally filtering through a Chamberland filter into sterile flasks (Croft Hill, Chem. Soc. Trans. 1898, 634), a neutral or faintly acid solution being thus obtained. The enzyme cannot be prepared in an active state by precipitation with alcohol (Fischer, Ber. 1894, 27, 1113; Röhmann, *ibid.* 3251), although alcohol does not affect the maltase content of dry yeast or the dried extract. It rapidly hydrolyses maltose into glucose, 1 c.c. of the extract prepared as described above decomposing 20 p.c. of the maltose in 20 c.c. of a 2 p.c. solution at 30° in 40 minutes. The synthetic action of this extract has already been discussed. The action of the enzyme is at once destroyed by free alkali. Maltase is very widely distributed, occurring in many yeasts (but not in *S. Marxianus* (Hansen), *S. exiguus* (Hansen), *Saccharomycodes Ludwigii* (Hansen), *S. apiculatus* (Rees), and the lactose-fermenting yeasts), in many bacteria and moulds, in the higher plants, and in the small intestine, liver, kidneys, blood, and other tissues of mammals. Maltase, as already mentioned, only hydrolyses α-glucosides, and is therefore sometimes called α-glucase. It does not affect *iso*maltose, which is a β-glucoside, or trehalose, which is, however, hydrolysed by a special enzyme, *trehalase*, which occurs in moulds, some yeasts, and in green malt.

Lactase is the specific enzyme which hydrolyses lactose into glucose and galactose. It also hydrolyses the β-alkylgalactosides, but not the α- compounds, and is therefore a β-enzyme. Its rate of action is diminished by galactose, but by no other sugar, and it therefore appears to combine with this substance as well as with lactose. Lactase occurs in a few yeasts, from which it may be extracted by grinding with glass powder and treatment with water (Fischer, Ber. 27, 2991, 3481) or by Buchner's process, but is best prepared by extracting kefir grains with water. It also occurs in some bacteria (*B. bulgaricus* (Grigoroff), &c.), and moulds (*e.g. Allescheria gayoni* (Sacc. & Syd.)) and in the small intestine of carnivorous and omnivorous animals and of young herbivora (Plimmer, J. physiol. Chem. 1906, 35, 20). An enzyme which decomposes lactose also occurs in the 'emulsin' obtained from almonds (H. E. and E. F. Armstrong and Horton, Proc. Roy. Soc. 1908, B, 80, 321), which probably differs from yeast lactase. Lactase, like maltase, effects the synthesis of a disaccharide, *iso*lactose (Fischer and Armstrong, Ber. 1902, 35, 3144).

Amylase or diastase. Enzymes capable of acting on starch with the production of a sugar appear to occur in nearly all living organisms. The whole question of the nature of these enzymes and of their action on starch is one of great complexity. The constitution of starch and of the dextrins formed from it being still unknown, no clear idea of the chemical action involved has been obtained, nor has any satisfactory criterion been found by which to judge whether only one or several enzymes are present. It is therefore impossible to do more in this place than give a very brief statement of the chief facts which have been ascertained. More complete information will be found in the article on BREWING, and in The Principles and Practice of Brewing, by Sykes and Ling (London, 1907).

The vegetable amylases or diastases are found in the germinating seeds and also in the leaves and other parts of the plant. The sources of the enzymes which have been chiefly investigated, are malt and the mould *Aspergillus oryzæ* (Ahlburg Cohn), the amylase of which is known as takadiastase. The enzyme is extracted from malt by treatment with water or dilute alcohol, and may be several times precipitated by alcohol and further purified by dialysis (Lintner), or by being salted out from aqueous solution by ammonium sulphate (Wroblewski). The greatest degree of purification appears to have been attained by Fraenkel and Hamburg (Hofm. Beitr. 1906, 8, 389), by adding a suitable amount of basic lead acetate, filtering, fermenting with yeast, and drying. This preparation was strongly active, and showed none of the albumin reactions except a very faint Millon's reaction. It appeared to contain two enzymes, one non-diffusible and the other diffusible. On the other hand, Wroblewski's purest diastase had all the properties of an albumose.

Starch paste is first liquefied by malt extract, and the starch is then rapidly converted at 50° into a mixture of maltose and dextrins, about 81 p.c. of the starch being converted into maltose, and 19 p.c. into dextrin. The further conversion of this dextrin into maltose proceeds extremely slowly (Brown, Heron, Morris). It appears to be undoubted that many complex dextrins intervene between starch and maltose, but their constitution is still unknown. The existence among the products of an *iso*maltose $C_{12}H_{22}O_{11}$ (Lintner), has been disproved (Ling and Baker). The action of diastase solution which has been heated to 68°–70°, is modified, so that less maltose and more dextrin are produced and more dextrin remains unchanged, whilst a certain proportion of glucose appears. This change in the mode of action of the enzyme may be due to an actual modification of the enzyme (Ling and Davis), but is regarded by many as evidence in favour of the theory (Wijsman, Beyerinck, Pottevin, Fraenkel, and Hamburg) that at least two enzymes are present, one of which produces dextrin and the other converts this into maltose. The separation of the enzyme into two parts by dialysis, one of which liquefies starch paste, and the other hydrolyses soluble starch, is also in favour of the existence of two enzymes. A different interpretation of the facts is due to Maquenne and Roux, according to whom starch contains two substances, *amylopectin*, to which the formation of the characteristic paste is due, and *amylose*, which is soluble. The amylose is converted by one enzyme of the diastase into maltose, whilst the amylopectin yields the dextrins under the action of a second enzyme. In mammals, diastatic enzymes are secreted by the salivary glands (ptyalin), the pancreas, and the intestine, and are also present in the liver, blood, muscular tissues, and most of the organs of the body. These enzymes convert starch and glycogen into maltose, but in many cases this is further changed into glucose by the maltase also present.

Emulsin. This name was originally applied by Liebig and Wöhler to the enzyme contained in almonds, which brought about the hydrolysis of amygdalin into hydrocyanic acid, benzaldehyde, and glucose. Further investigations (H. E. and E. F. Armstrong and Horton, Proc. Roy. Soc. 1908, B, 80, 321; Rosenthaler, Biochem. Zeitsch. 1910, 28, 408) have shown that the 'emulsin' of these workers contains a large number of distinct enzymes, and that the hydrolysis of amygdalin is a very complex phenomenon. It is most probable that the complete decomposition of this compound involves at least three enzymes, each capable of bringing about one stage in the reaction. Amygdalin has probably the formula

$$C_6H_5\cdot CH(CN)\cdot OC_6H_{10}O_4\cdot O\cdot C_6H_{11}O_5,$$

the glucose molecule being combined with the benzaldehyde residue to form a β-glucoside and the terminal glucose group as an α-glucoside. The stages of the hydrolysis are probably:

(1) Hydrolysis by *amygdalase*, forming α-glucose and *l*-mandelonitrile-β-glucoside

$$C_6H_5\cdot CH(CN)\cdot O\cdot C_6H_{10}O_4\cdot O\cdot C_6H_{11}O_5+H_2O = C_6H_5\cdot CH(CN)\cdot O\cdot C_6H_{11}O_5+C_6H_{12}O_6.$$

(2) Hydrolysis of this compound by a *β-glucosidase* into β-glucose and *d*-benzaldehyde-cyanhydrin

$$C_6H_5\cdot CH(CN)\cdot O\cdot C_6H_{11}O_5+H_2O = C_6H_5\cdot CH(OH)\cdot CN+C_6H_{12}O_6.$$

(3) Decomposition of the cyanhydrin by *δ-hydroxynitrilase*

$$C_6H_5\cdot CH(OH)\cdot CN = C_6H_5\cdot CHO+HCN.$$

The crude emulsin also effects the synthesis of *d*-benzaldehydecyanhydrin from benzaldehyde and hydrocyanic acid; but Rosenthaler (Biochem. Zeitsch. 1908, 14, 238; 1909, 17, 257) does not regard this as a reversed action of the enzyme, but as due to a different enzyme, and claims to have separated the two.

Amygdalase is, at all events in some cases, present in yeast (Henry and Auld, Proc. Roy. Soc. 1905, B, 76, 568); and Emmerling (Ber. 1901, 34, 600, 2206, 3810) has observed the synthetic production of amygdalin from *l*-mandelonitrile-glucoside and glucose in presence of crude yeast maltase. Emulsin also contains a lactase, to which reference has already been made.

Crude emulsin occurs in sweet almonds, from which it is extracted by digestion with chloroform water, and can be precipitated by alcohol. It is also found in many moulds as well as in yeast. The β-glucosidase also occurs in many bacteria (Twort, Proc. Roy. Soc. 1907, B, 79).

The β-glucosidase of emulsin hydrolyses the β-alkyl-glucosides and many of the natural glucosides, such as arbutin, salicin, prulaurasin, æsculin, and many others.

Other glucosidoclastic enzymes are myrosin, which hydrolyses the sinigrin of mustard, and tannase which decomposes the natural tannins, and many more. Of considerable technical importance is the action of the enzyme contained in the leaf of the indigo plant, which is termed satase or indimulsin, and converts the indican of the leaf into glucose and indoxyl, the latter being then converted by oxidation into indigotin.

Many other specific glucoside enzymes are known (*see* The Simple Carbohydrates and Glucosides, by E. F. Armstrong, London, 1910).

The digestive enzymes comprise a great number of hydrolytic agents capable of replacing the $-NH_2$ group by $-OH$ (amidases or desamidases) or of causing the decomposition:

$$R{\cdot}NH{\cdot}COR' + H_2O = R{\cdot}NH_2 + R'{\cdot}COOH$$

to which the hydrolysis of the proteins appears to be mainly due. These are classed according to the completeness of the decomposition produced and the complexity of the compounds attacked under the various heads already given.

1. *Amidases or desamidases*, the most important of which accelerate the hydrolysis of urea and the conversion of adenine into hypoxanthine, and guanine into xanthine. Similar changes are often produced by micro-organisms (*see Alcoholic fermentation, Ammoniacal fermentation of urea*, and *Putrefaction*).

These enzymes have not hitherto been separated from accompanying hydrolytic enzymes of different character with which they occur in many animal tissues and organs.

2. *Enzymes capable of hydrolysing various comparatively simple nitrogenous substances.* Among these are arginase (Kossel and Dakin, Zeitsch. physiol. Chem. 1904, 41, 321; 42, 181), creatinase, and the nucleases.

3. *Peptases and ereptases.* The synthetic production of the polypeptides by Fischer has rendered it possible to obtain a very large amount of information with respect to the nature and limitations of action of the proteoclastic enzymes, a line of research which has chiefly been followed by Fischer and Abderhalden (Lehrbuch physiol. Chem. Berlin, 1909). The relations appear to be very complex, and no approach to finality in the matter has yet been made.

Trypsin itself decomposes many albumins down to the stage of polypeptides, and some of the latter are resolved into amino-acids, whereas others resist the further action of the enzyme, and are found in the digested liquid.

In the blood, in all the organs and tissues, and in the intestinal juice are found enzymes which hydrolyse polypeptides, but are without action on the albumins. The relation to the polypeptides is highly specific, some which are resistant to trypsin being decomposed, some which are hydrolysed by trypsin being unaffected. Of the synthetical polypeptides, only those which contain the naturally occurring optical isomerides of the amino-acids are decomposed.

Only a very careful and thorough examination of the question will reveal how far the hydrolysis of various polypeptides is due to the action of different enzymes, and give some idea of the degree of complexity of these digestive 'enzymes.'

The decomposition of simple compounds, such as the dipeptides, alanyl-alanine, glycyl-glycine, and glycyl-tyrosine, provides an admirable opportunity for studying the kinetics of enzyme action. Much the same general conditions are revealed as in the case of invertase, but little work has as yet been done along these lines.

4. *Enzymes capable of hydrolysing the albumins.* (*a*) *Trypsin or tryptase.* This name belongs specifically to the enzyme secreted in the inactive (zymogen) form by the pancreas, as already described, but is applied, as a general term, to a large number of enzymes, both of animal and vegetable origin, which attack albumins and produce from them amino-acids or comparatively simple polypeptides. Among the most important of these are the leucotryptase of the leucocytes of the blood, the autoclastic enzymes of animal tissues and organs, and the proteoclastic enzymes of the lower animals. In the vegetable kingdom, many similar enzymes occur, notably *Papayotin* in the melon tree, *Carica papaya* (Linn.); *bromelin* in the pineapple, as well as the *endotryptases* of yeast, and many bacteria.

Pancreas trypsin is most active in presence of alkalis, the exact optimum concentration being different for various preparations, 0·2 p.c. of sodium carbonate being commonly employed. It also exerts a certain amount of action in very weak acid solution. The amount of hydrolysis is proportional to the amount of enzyme and the time of action, the concentration being indifferent (Löhlein, Hofm, Beitr. 1905, 7, 120; Hedin, J. physiol. 1904, 32, 468; 1906, 34. 370).

Trypsin is readily taken up, probably by adsorption, by fibrin, and can thus be removed from solution. It is also adsorbed by animal charcoal and cannot be re-extracted from this substance by water (Hedin).

Substances which tend to inhibit the action of the enzyme and are termed antitrypsins, occur in blood serum, in parasitic worms, and in yeast, but the nature and function of these is as yet little understood (*see* Hedin, Zeitsch. physiol. Chem. 1907, 52, 412; Buchner and Haehn,

Biochem. Zeitsch. 1910, 26, 171; Weinland, Zeitsch. Biol. 1902, 44, 1, 46).

(*b*) *Pepsin or pepsinase.* This enzyme is the characteristic digestive agent of the gastric juice of all vertebrates. It is also secreted by Brunner's glands in the intestine, and occurs in a few flesh-eating plants, such as the various species of *Nepenthes* (pitcher plant), *Dionœa* and *Drosera* (sundew). The most characteristic properties of pepsin are that it only acts in acid solution, and that it does not hydrolyse any known polypeptide. It converts the albumins (phosphoproteins, nucleoproteins, gelatin, &c.) probably first into acid albumins and then into simpler compounds of unknown constitution. These were formerly classed as albumoses, precipitable by ammonium sulphate; and peptones, non-precipitable by this salt, but precipitable by phosphotungstic acid. The nature and individuality of the numerous compounds of these classes which have been described are still involved in obscurity, and all that can be said with certainty is that hydrolysis does not go so far as to produce simple amino-acids. The least impure form of pepsin appears to have been obtained by Pekelharing (Zeitsch. physiol. Chem. 1902, 35, 8), who simply dialysed the filtered gastric secretion of a dog, obtained by fistula, and then dried the washed precipitate thus produced. The pepsin is deposited in perfectly transparent spheres, containing very little ash, and is quite free from phosphorus. When hydrolysed with acid, it yields a pentose, purin bases, and an acid, termed pepsinic acid, which gives the albumin reactions.

According to Schütz, the rate of hydrolysis is proportional to the square root of the amount of the pepsin (Zeitsch. physiol. Chem. 1887, 9, 377). This is explained by Arrhenius as due to the inhibiting effect of the products of the hydrolysis and by Bayliss as due to the fact that the combination between the pepsin and the substrate is of the nature of adsorption. When the enzyme acts on coagulated albumin, the effect, however, appears to be proportional to the concentration. The optimum temperature appears to be 40°, whilst the rate of action is greatly influenced by the concentration of the hydrogen ions present, the optimum being, according to Sörensen, 10^{-2}.

Antipepsins are said to exist in the mucous membrane of the stomach, and to prevent the autodigestion of the organ. These are probably also present in commercial pepsin and rennet. The relations between pepsin and rennet are discussed under the heading of *Rennet*.

Enzymes producing Oxidation.

In spite of the fact that both the higher plants and all animals supply themselves with energy exclusively by the oxidation of their various food materials by atmospheric oxygen, with the ultimate production of carbon dioxide and water, practically nothing is known of the mechanism by which this oxidation is brought about or of the chemical changes involved.

On the other hand, it has been found that many animal and vegetable cells secrete materials which can be obtained in the form of press juice or extract by the aid of which various specific oxidations can be effected. The most completely investigated of the changes of this kind is the oxidation of phenols and allied compounds to quinones or colouring matters, which is produced by many vegetable cells and is exemplified by the production of a brown colouration when many fruits are cut open and exposed to the air, and of a blue colour when certain fungi are broken (*Russula, Agaricus*).

The nature of these oxidising systems has been to a considerable degree elucidated by the researches of Bach and Chodat (Biochem. Zentr. 1903, 1, 417, 457), according to whom the oxidation involves the co-operation of two agents. One of these has the properties of an enzyme (*i.e.* it is a thermolabile colloidal catalyst), and has the function of catalysing the reaction between a peroxide, either hydrogen peroxide or an organic peroxide, and the oxidisable matter; this enzyme is accordingly known as a *peroxidase*. The second agent may consist of (*a*) hydrogen peroxide, (*b*) an organic peroxide. In the former case, the oxidation is effected by the oxygen of the hydrogen peroxide and ceases as soon as this has been expended. In the second case, the organic peroxide gives up its oxygen to the oxidisable substance, and is then reformed by the combination of the residue with the oxygen of the air, so that a continuous oxidation occurs. These organic peroxides were termed *oxygenases* by Bach and Chodat, but this term is at variance with the present system of nomenclature, and is best replaced by the expression peroxide (Oppenheimer) or complex peroxide. The peroxidase is often found alone, unaccompanied by peroxide, and its presence can then only be detected by adding hydrogen peroxide as well as a substance to be oxidised. When both peroxidase and peroxide occur together (as in *Russula, Lactarius*, &c.), the system is often termed an *oxidase*. In certain cases, the peroxide and peroxidase can be separated by fractional precipitation with alcohol, and it was in this way that Bach and Chodat ascertained the foregoing facts.

The tests used for the detection of peroxidases and oxidases are, as a rule, identical, but when only peroxidase is present the addition of hydrogen peroxide is necessary. Some of the most generally used are as follows: (1) A blue colouration is produced with a freshly prepared alcoholic tincture of guaiacum resin. The use of this test for the detection of an oxidase requires great care, as a peroxide is readily formed in the alcoholic tincture itself which reacts with the peroxidase; it is therefore better to employ guaiaconic acid, which is free from this defect. (2) A dark-blue colouration is produced with *p*-phenylenediamine. (3) Dark-coloured purpurogallin is produced from pyrogallol. (4) By far the most satisfactory test for the presence of an oxidase is the direct measurement of the oxygen absorbed. (5) A test applicable only for peroxidase is the oxidation of formic acid to carbon dioxide and water in presence of peroxide of hydrogen or ethylhydroperoxide (Batelli and Stern, Biochem. Zeitsch. 1908, 13, 44).

Nature of peroxidase. Many interesting suggestions have been made as to the nature of the peroxidases. It was early pointed out (Bertrand, Compt. rend. 1897, 124, 1355) that oxidising extracts usually contained manganese

or iron, and that the possibility existed that these mineral substances, perhaps in combination with proteins, might, by alternate oxidation and reduction, produce the effects observed, just as ferrous sulphate greatly modifies and increases the action of hydrogen peroxide (Fenton). Dony-Hénault (Bull. Acad. Belg. 1908, 105) has, in fact, prepared a colloidal suspension of oxide of manganese in gum arabic which has the properties of laccase (*q.v.*), and can be precipitated by alcohol and redissolved without losing these powers; whilst Euler and Bolin (Zeitsch. physiol. Chem. 1908, 57, 80) found that manganese salts, in presence of sodium salts of organic hydroxy-acids, produced analogous effects. Somewhat similar mixtures, containing colloidal iron salts, also act in many ways like the peroxidases (de Stoecklin, Compt. rend. 1908, 147, 1489; Wolff, *ibid.* 1908, 146, 142, 781, 1217). It seems probable, however, that the peroxidases of vegetable and animal origin contain a factor which determines their specific character, although it is possible, but not certain, that manganese or iron compounds may play some part in the action of certain of them. The chief types of oxidising enzymes known are the following:—

1. **The peroxidases**, which occur in all parts of plants. Their occurrence in animal tissues is difficult to establish, as blood produces all the reactions ascribed to peroxidases, and must therefore be absent before the presence of the latter can be proved (Batelli and Stern, Biochem. Zeitsch. 1908, 13, 44).

2. **The enzymes producing coloured compounds** from **aromatic phenols**, &c. These may be known as phenolases (a term which is, however, used by Oppenheimer in a more restricted sense). They produce the most varied oxidations, accompanied by colour changes, and are frequently highly specific. The work of Bach and Chodat, discussed above, applies to certain of these enzymes, but its applicability to tyrosinase has not yet been proved.

Laccase occurs in the juice of the lac tree of Tonkin (*Rhus vernicifera* (D.C.)), and brings about the oxidation of the yellow juice to the black lacquer (Yoshida, Chem. Soc. Trans. 1883, 43, 472; Bertrand, Compt. rend. vols. 118–122), and has also been found in many other phanerogams (lucerne, cabbage, potatos, &c.) and in fungi. It accelerates the oxidation of *o*- and *p*-polyphenols (but not of *m*- compounds), and has no effect on tyrosine. Its solutions only lose their oxidising powers slowly when boiled.

Tyrosinase. Enzymes capable of oxidising tyrosine with production of coloured substances occur widely, both in the animal and vegetable kingdoms, frequently accompanied by laccase. According to Gortner (Chem. Soc. Trans. 1910, 110), both soluble and insoluble forms of tyrosinase occur in the meal worm (*Tenebro molitor*). The insoluble form contains iron, but no manganese, and is capable of oxidising a relatively large amount of tyrosine, producing a series of colour changes through pink, rose, violet, and blue-black to black (*melanin*). It also effects the oxidation of *p*-aminophenol, guaiacol, gum guaiacum, and 2:4-diaminophenol, but not of quinol or pyrogallol. Tyrosinase also occurs in many leaves, which become black on drying, and in bran, in which it is unaccompanied by laccase. The blue colour observed when certain mushrooms are broken is not due to the action of this enzyme but to that of laccase (Bertrand). A very large number of *p*-hydroxy phenyl derivatives, as well as nearly all derivatives of tyrosine, tryptophane, and some of its derivatives, adrenalin, phenol, and *p*-cresol are oxidised.

An enzyme also occurs in the animal tissues, which produces indophenol from α-naphthol and *p*-phenylenediamine, a reaction not given by tyrosinase or laccase.

3. **Aldehydase.** The liver, lungs, and spleen of animals contain an oxidase capable of converting certain aldehydes (salicylaldehyde, formaldehyde) and benzyl alcohol into the corresponding acids (*see* Jacoby, Virchow Arch. 1899, 157, 235; Zeitsch. physiol. Chem. 1900, 30, 135; 1901, 33, 128). It can be purified by treatment with dilute alcohol, and is very sensitive to acids and alkalis. It is doubtful whether it is accompanied by a peroxide (Abelous and Aloy, Compt. rend. Soc. Biol. 1903, 52, 891).

4. The various oxidative fermentations brought about by micro-organisms are discussed later.

Catalase. This name was given by Loew (Bull. Agric. Washington, 1900) to the enzyme which has the power of catalysing the decomposition of hydrogen peroxide into water and oxygen. It has long been known that animal and vegetable tissues have the property of producing this decomposition, and, at one time, this was thought to be a general characteristic of all enzymes (Schönbein, J. pr. Chem. 1863, 89, 334). Further investigation, however, showed that this was not the case, but that this property belonged to a special, very widely distributed enzyme (Loew). The power of decomposing hydrogen peroxide is possessed by all the tissues of the animal body, and is most marked in the liver. Thus it was found by Batelli and Stern (Arch. Fisiolog. 1905, 2, 471) that 0·1 gram of guinea-pig liver evolved 5800 c.c. of oxygen from 1 p.c. hydrogen peroxide at 37°, whilst the corresponding number for the blood was 490 c.c., and for the muscle 34 c.c. The enzyme can be concentrated by extracting the tissue with water, precipitating with alcohol, extracting this with water, and again precipitating with alcohol. A similar process applied to blood yielded a clear faintly yellow solution of the enzyme, free from blood and from iron (Senter, Zeitsch. physikal. Chem. 1903, 44, 257; 1905, 51, 673). Preparations can be obtained from many plant tissues in a similar manner, as well as from yeast and many fungi. It is not certain whether the enzymes derived from these various sources are identical, but Loew has distinguished the soluble and insoluble forms of the enzyme obtained by him from tobacco as β- and α-catalase, and Senter has named the enzyme from blood hæmase.

The catalytic function of the enzyme appears to be strictly limited to the decomposition of hydrogen peroxide. The oxygen is liberated in the gaseous state, and does not effect any oxidations other than can be brought about by free oxygen. The enzyme is very sensitive to the presence of free hydrogen ions, and, according to Sörensen, acts best in neutral solution, whilst alkalis and many salts exert an inhibiting effect.

Hydrocyanic acid is a powerful inhibitant, but does not cause any permanent change in the enzyme. Hydrogen peroxide itself exerts a destructive action on the enzyme, and hence accurate measurements of the rate or amount of decomposition can only be made in dilute solution and in presence of a relatively large amount of enzyme. Under these conditions, the decomposition is monomolecular, and the velocity is proportional to the concentration of enzyme and of hydrogen peroxide, whilst with increasing concentration of hydrogen peroxide the velocity becomes relatively slower (Senter). As the oxygen appears to be produced in the molecular form, it is probable that the decomposition occurs in stages, either an intermediate compound of enzyme and hydrogen peroxide being formed which then breaks down, or a compound of the enzyme and oxygen which then reacts with a second molecule of the peroxide.

The reaction is analogous in many respects to the decomposition of hydrogen peroxide by colloidal platinum (Bredig). The catalase is, however, more efficacious, a solution of 0·001 gram per litre of catalase-containing material from blood having the same effect as a solution of colloidal platinum containing 0·006 gram (Euler, Hofm. Beitr. 1906, 7, 1).

The action of catalase is measured either by titration of the hydrogen peroxide present at various stages of the reaction or by direct measurement of the oxygen evolved. Estimations of the rate or extent of decomposition of hydrogen peroxide by the catalase of milk or of malt (van Laer) have been used in the analytical examination of these materials. A solution of vegetable catalase is used to remove the excess of hydrogen peroxide from cream which has been sterilised by the addition of this substance (Budde).

The physiological function of catalase in the animal body is unknown, but it is conjectured that it may be to decompose hydrogen peroxide or complex peroxides formed during processes of oxidation. In the green parts of plants, the catalase decomposes the hydrogen peroxide, which is formed along with formaldehyde, by the photochemical reduction of carbon dioxide in presence of chlorophyll (Priestly and Usher)

$$CO_2 + 3H_2O = H{\cdot}CHO + 2H_2O_2.$$

The Coagulases.

A number of enzymes exist which have the property of bringing about changes in various liquids which result in the formation of an insoluble material. The most important of these are:

(1) The production of a curd in milk by the enzyme of rennet (chymase).

(2) The coagulation of the blood by the enzyme thrombase.

(3) The coagulation of muscle.

(4) The formation of the insoluble pectic acids from the pectin substances of plants (pectase).

Most of these changes are exceedingly complicated, the coagulation of the blood being one of the most complex phenomena in the whole range of physiological chemistry. The only one which can be treated here is the action of rennet on milk.

Rennet, or chymase. Enzymes possessing the power of coagulating milk occur in the form of zymogen in the mucous membrane of the stomach of many animals, and are secreted into the gastric juice; similar substances are also found in many plants. Rennet is usually prepared by digesting the membrane of the stomach of the calf with 0·1–0·2 p.c. hydrochloric acid, or with glycerol or salicylic acid, and can be precipitated by alcohol. Some doubt exists as to the relation of rennet to pepsin, which is also secreted by the cells of the mucous membrane of the stomach. According to Pawlow (Zeitsch. physiol. Chem. 1904, 42, 415), the coagulation of milk is an effect of the action of pepsin under special conditions, whereas Hammarsten strongly supported the view that the two enzymes are distinct (Maly's Jahresb. 1872, 1874, 1877). The question is a very complex one, owing to the existence of antipeptic and anti-rennet substances in the stomach extracts, but the balance of opinion now inclines to the belief that two independent enzymes exist.

Rennet converts the caseinogen of milk into casein, the change most probably (but not certainly) consisting in the hydrolytic decomposition of the molecule of caseinogen with production of casein and an albumose. The casein thus produced is precipitated by calcium salts as an insoluble curd, and it is the formation of this precipitate which is observed in the curdling of milk by rennet. Solutions of rennet in the minimum amount of lime water or in caustic soda solution are not curdled by rennet, but after treatment give a precipitate with calcium salts.

The time required for curdling is proportional both to the concentration of enzyme and of caseinogen. The action is favoured by slight acidity and hindered by alkalinity. The optimum temperature is 37°–45° and the temperature coefficient of the reaction is about 3 for 10°. When the milk is boiled before being treated, the formation of curd is interfered with, probably owing to changes produced in the calcium salts of the milk. The enzyme is capable of curdling at least 1,000,000 times its weight of milk.

ALCOHOLIC FERMENTATION.

The production of carbon dioxide and alcohol from sugar is by far the most important of all technical processes of fermentation, and has, therefore, been more thoroughly investigated than any other change produced by micro-organisms. Although both alcohol and carbon dioxide are produced from sugar by many micro-organisms belonging to the class of bacteria, the power of bringing about the typical alcoholic fermentation, of decomposing sugar almost quantitatively into these two substances, is possessed among micro-organisms only by certain moulds and by a group of unicellular fungi which belong to several closely allied families and are commonly grouped together as yeasts. The biology and mode of culture of these are treated in the article on BREWING.

Composition of yeast. The cell consists of membrane, cytoplasm, and nucleus, but much doubt exists as to the exact form of the nucleus and the changes which it undergoes during fermentation, budding, and spore formation. In the cytoplasm occur vacuoles, and at various stages in the life of the cell granules of chroma-

tin and volutin are formed as well as fat droplets and glycogen.

Yeast, which has been pressed at about a half-ton per square inch, forms a friable, almost white mass, containing about 70 p.c. of water and alcohol, and 30 p.c. of solids. The composition of the dry matter of yeast varies so greatly with conditions of growth, &c., that no general statement is of much value. The ash, which amounts to 5–10 p.c. of the dry residue, consists essentially of potash (K_2O, 28–39 p.c.), magnesia (MgO, 4–6 p.c.), lime (CaO, 1–7 p.c.), and phosphoric oxide (P_2O_5, 45–59 p.c.), together with smaller quantities of sulphur trioxide, iron, silica, and traces of chlorine. The exact nature of the cell membrane is as yet undecided, but it appears to be closely allied to cellulose, although true cellulose is absent. The cytoplasm contains a coagulable albumin, a nuclein, glycogen, yeast gum, and a large number of other compounds, in part derived from these by hydrolysis.

General phenomena of alcoholic fermentation. 1. *The fermentable substances.* All yeasts which ferment glucose also ferment mannose and lævulose. The case of galactose is different, as some yeasts appear to ferment it imperfectly, and others not at all. It has been found by many observers and may now be regarded as established, that certain yeasts which do not normally ferment galactose readily acquire this property when they are cultivated in the presence of this sugar, as for example in hydrolysed lactose. Examples of this are *S. carlsberg* (H.), *S. cerevisiæ* (H.), *S. thermantitonum* (Johnson), &c. Indeed, according to Lindner, all the culture yeasts exhibit this property (*see* Slator, Chem. Soc. Trans. 1908, 217; Lindner, Wochensch. Brauerei, 1911, 28, 61).

The higher saccharides are not directly fermentable by yeast, but must first undergo hydrolysis to the simple hexoses. This is effected by hydrolytic enzymes present in the yeast, which can, as a rule, be extracted from the cell by appropriate methods. The ordinary culture yeasts employed in brewing, &c., contain maltase and invertase, but not lactase, and are therefore able to ferment maltose and cane sugar, but not lactose. Bottom yeasts appear invariably to contain melibiase, which decomposes melibiose into glucose and galactose, whilst this enzyme is lacking in top yeast. An analytical method for detecting bottom yeast in top yeast has been founded on this fact. In addition to this, practically all culture yeasts are able partially to ferment raffinose, which on hydrolysis yields melibiose and fructose, and they probably contain a special enzyme, *raffinase*, which produces this hydrolysis, although it is possible that this is due to the invertase. In the case of top yeasts, only the fructose thus produced undergoes alcoholic fermentation, the melibiose remaining unaltered, whereas the bottom yeasts decompose this also. Dextrin is also more or less slowly fermented by yeast, the hydrolysis being effected by a dextrinase or amylase. This property is of great importance in brewing, as a yeast which possesses a comparatively large amount of this enzyme is able to attenuate the wort to a greater extent, and to produce a larger yield of alcohol. Starch and glycogen are unaffected by yeast, probably because, owing to their highly colloidal nature, they are unable to penetrate the cell. Species of yeast are now known which are lacking in one or other of all these hydrolytic enzymes, and hence are incapable of fermenting the corresponding sugar. These have frequently been employed for the isolation of such a sugar as maltose from mixtures containing glucose or fructose, and in fact their relations to the disaccharides are employed as a means of classification. Thus *S. marxianus* (H.) and *S. exiguus* (H.) ferment cane sugar, but not maltose; *S. rouxi* (Boutroux) ferments maltose, but not cane sugar; *S. fragilis* (Jörg), found in kefir, ferments lactose, and *S. mali* (Duclaux) only ferments the simple sugars and is without action on the disaccharides. No yeast appears to be able to ferment the synthetical disaccharides, such as *iso*maltose or glucosidogalactose, and this disability extends to the isomerides of the hexoses, such as sorbose, tagatose, &c., to the optical antipodes of the fermentable sugars which have been obtained by synthesis, and to the pentoses and tetroses. Beyond the simple sugars mentioned above, no other substance appears to be directly fermentable by yeast to alcohol and carbon dioxide, with the exceptions of a synthetical 9-carbon atom sugar and of glyceraldehyde and dihydroxyacetone, which, according to Bertrand and Buchner and Meisenheimer (Ann. Chim. Phys. 1904, [8] 3, 181; Ber. 1910, 43, 1773), are slightly acted on by yeast. Glycerol, lactic acid, and the higher alcohols such as mannitol and dulcitol, are not fermented. According to Neuberg, pyroracemates, lactates, glycerates and the salts of many α-ketonic acids are decomposed by yeast with production of carbon dioxide (Biochem. Zeitsch. 1911, 31, 170; 32, 323).

2. *The rate of fermentation by yeast* has been investigated by many authors. It is best examined by Slator's method of adding a suspension of yeast to the solution to be fermented, and determining the initial rate of fermentation. In this way, all errors due to change in the amount and condition of the yeast and to the influence of the products of decomposition are, to a large extent, avoided (Chem. Soc. Trans. 1906, 128). By this and other methods, it has been established that (1) the rate of fermentation is directly proportional to the number of yeast cells present; (2) the rate of fermentation increases with the concentration of the sugar up to a certain limit, and then remains approximately constant, decreasing slightly as the concentration is further augmented.

Working with a suspension of 40,000,000 cells per c.c. at 30°, Slator found that the rate was almost constant for glucose concentrations between 0·5 and 10 grams per 100 c.c. The mode of action of yeast is therefore identical with that typical of enzymes which has already been discussed.

The rate increases with the temperature, but the temperature coefficient diminishes as the temperature increases. The following values were obtained by Slator for glucose; they are independent of the concentration of yeast and glucose, the class of yeast and presence and absence of nutrient materials remaining the same when inhibiting agens are present:—

Temp.	V_{t+10}/V_t
5°	5·6
10°	3·8
15°	2·8
20°	2·25
25°	1·95
30°	1·6

The temperature coefficient for an ordinary chemical reaction is of the same order as these numbers, viz. 2–3 for 10°.

Glucose and fructose are fermented at the same rate, and this is also the case when the fermenting power of the yeast is partially destroyed by heat, antiseptics, &c. On the other hand, mannose and galactose may be fermented at a different rate from glucose, and the rates are differently affected by inhibiting agents. The temperature coefficients for fructose and mannose are the same as for glucose, that for galactose is slightly less.

3. *Heat of fermentation.* During the fermentation of sugar by yeast, a considerable amount of heat is evolved, so that the temperature of the mass rises as the fermentation proceeds. The quantity of heat evolved may be calculated from the difference between the heat of combustion of glucose (675·7 Cals.) and that of the alcohol formed from it ($2 \times 325{\cdot}7 = 651{\cdot}4$ Cals.), the remaining product, the carbon dioxide, being completely oxidised. This difference amounts to 22·3 Cals., so that the fermentation of 180 grams of glucose liberates enough heat to raise the temperature of 22 litres of water 1°. This theoretical number has been confirmed by the experiments of Bouffard (Compt. rend. 1895, 121, 357), who obtained the value 23·5 Cals. In the fermentation of a disaccharide, heat is also evolved by the hydrolysis to the simple sugars; but this is small in amount, being 4·5 Cals. for cane sugar and 3·8 Cals. for maltose (Herzog, Zeitsch. physiol. Chem. 1903, 37, 383), so that the numbers actually observed for these sugars per gram-molecule are approximately twice that for glucose (Rubner, Arch. Hygien. 1904, 48, 260; 49, 355; A. J. Brown, J. Inst. Brewing, 1901, 7, 93).

4. *Products of fermentation.* The earlier observers (Lavoisier, Gay-Lussac) considered that in the process of fermentation the sugar was completely decomposed into carbon dioxide and alcohol, according to the equation:

$$C_6H_{12}O_6 = 2CO_2 + 2C_2H_6O.$$

Schmidt, in 1847, however, observed the occurrence of succinic acid in all fermented liquors, and the amount of this substance formed was carefully estimated by Pasteur (Compt. rend. 1858, 46, 857), who also made the important observation that glycerol was an invariable product of the fermentation of sugar. According to Pasteur, the products from 100 parts of cane sugar, which yield 105·36 parts of invert sugar, are:

Alcohol	51·11
Carbon dioxide	49·42
Succinic acid	0·67
Glycerol	3·16
Cellulose, fat, and extractive matter	1·00
	105·36

The proportions of these products were subsequently found to be variable and to depend on the condition of the yeast, the nature of the nutrient material, &c. Many other subsidiary products have now been recognised in addition to succinic acid and glycerol. Among these may be mentioned *iso*butyleneglycol (in wine and cherry brandy), formic acid, acetic acid, propionic acid; butyric acid, and several still higher acids, which occur as esters (caproic, caprylic, pelargonic, capric, œnanthylic), and formaldehyde, acetaldehyde, and traces of higher aldehydes, propyl alcohol, *n*-butyl alcohol, *iso*butyl alcohol, *n*-amyl alcohol, *iso*-amyl alcohol, ethylmethylcarbinol, and alcohols containing 6, 7, and 9 carbon atoms.

The alcohols and aldehydes mentioned above are found in the spirit obtained by the distillation of the fermented liquids. All such spirit yields a fraction of high boiling-point, which amounts to 0·1–0·7 p.c. of the whole, and is known as fusel oil (*q.v.*). The discussion which has long raged over the origin of this fusel oil has been set at rest by the researches of Ehrlich (Zeitsch. Rüb. Zuck. Ind. 1905, 539; Biochem. Zeitsch. 1906, 2, 52; 1909, 18, 391; Ber. 1906, 39, 4072), who has proved in the most conclusive manner that the higher alcohols and probably the corresponding acids and aldehydes which are observed in fermented liquids are formed by the yeast, not from the sugar, but from the amino-acids produced by the hydrolysis of the proteins of the medium and of the yeast cell itself.

The reaction is a general one, and requires the presence of living yeast and sugar as well as the amino-acid. Under these circumstances, the yeast not only ferments the sugar to alcohol and carbon dioxide in the usual way, but also brings about what Ehrlich terms the alcoholic fermentation of the amino-acids, according to the equation:

$$R{\cdot}CH(NH_2){\cdot}COOH + H_2O = R{\cdot}CH_2{\cdot}OH + NH_3 + CO_2.$$

The ammonia appears to be invariably assimilated by the yeast and is not found in the medium. This fact probably affords the key to the biological significance of the reaction. It is by means of this change that the yeast acquires the nitrogen necessary for its existence from the amino-acids, which are usually the chief available source of this element. The whole change is rendered possible by the utilisation of some of the energy evolved by the fermentation of sugar, which is proceeding simultaneously. Ehrlich has shown, by careful experiments, that in this way, leucine

$$(CH_3)_2{\cdot}CH{\cdot}CH_2{\cdot}CH(NH_2){\cdot}COOH$$

yields the *iso*-amyl alcohol

$$(CH_3)_2{\cdot}CH{\cdot}CH_2{\cdot}CH_2(OH)$$

and *iso*leucine $C_2H_5{\cdot}CH(CH_3){\cdot}CH(NH_2){\cdot}COOH$ the *d*-amyl alcohol $C_2H_5{\cdot}CH(CH_3){\cdot}CH_2{\cdot}OH$, which are the main constituents of fusel oil.

The other amino-acids yield corresponding products, tyrosine

$$OH{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH(NH_2){\cdot}COOH$$

being converted into *p*-hydroxyphenylethyl alcohol or tyrosol $OH{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH_2{\cdot}OH$, a substance of intensely bitter taste and phenylalanine $C_6H_5{\cdot}CH_2{\cdot}CH(NH_2){\cdot}COOH$ into phenylethyl alcohol $C_6H_5{\cdot}CH_2{\cdot}CH_2{\cdot}OH$, one of the chief constituents of oil of roses. It is almost

certain that many of the substances which impart flavour, bouquet, and aroma to fermented liquors have their origin in this manner, so that the subject is one of fundamental importance for the technologist.

Succinic acid is also formed by a reaction of this kind, which differs from the foregoing in so far as it involves an oxidation. The source of this substance is glutamic acid

$$COOH\cdot CH_2\cdot CH_2\cdot CH(NH_2)\cdot COOH,$$

which, instead of yielding γ-hydroxybutyric acid, as might have been expected, is converted into succinic acid

$$COOH\cdot CH_2\cdot CH_2\cdot CH(NH_2)\cdot COOH + 2O = COOH\cdot CH_2\cdot CH_2\cdot COOH + CO_2 + NH_3.$$

Yeast is, moreover, not only capable of producing these changes in amino-acids naturally present in the medium or purposely added to it, but also decomposes in a similar manner the amino-acids formed by the hydrolysis of its own albumin. Some of the cells evidently utilise the products of the autolysis of others which have died, and hence it comes about that even when a pure sugar solution is fermented by pure washed yeast, the fermented liquid contains a certain small proportion of fusel oil, succinic acid, &c. The amounts produced in these circumstances are, however, small, as they are also when the yeast is grown in presence of ammonium salts. It also follows from this that when yeast is grown in a synthetic medium, containing ammonium salts only as the source of nitrogen, the carbon of any fusel oil or succinic acid produced is indirectly derived from the sugar.

It seems probable, from the experiments of Neubauer and Fromherz (Zeitsch. physiol. Chem. 1911, 70, 326), that the amino-acid (I.) first undergoes indirect oxidation to the corresponding ketonic acid (III.) and ammonia, and that the acid is then decomposed by the yeast (in presence of sugar), forming carbon dioxide and an aldehyde (IV.), which then either undergoes reduction to an alcohol (*e.g.* fusel oil) or oxidation to an acid (*e.g.* succinic acid).

R	R	R	R
C<H, NH$_2$	C<OH, NH$_2$	CO	CHO
COOH	COOH	COOH	
I.	II.	III.	IV.

It is interesting to note that the reaction proceeds asymmetrically as already described (*see Enzyme action*).

So far no other origin than the sugar has been definitely proved for the glycerol, which is invariably formed during fermentation, and, unlike the substances discussed above, is equally produced by yeast juice and zymin, in the absence of living yeast. It has, however, been suggested that it arises from the decomposition of lipoid substances or of the nuclein of the cell.

The production of by-products is influenced not only by the nature of the available nitrogen supply, as already explained, but also by many other factors. Thus, Ashdown and Hewitt (Chem. Soc. Trans. 1910, 636) have adduced evidence to show that in the presence of formates the amount of aldehyde produced diminishes.

5. *Ratio of alcohol to carbon dioxide.* All these decompositions have an influence on the ratio of alcohol to carbon dioxide produced by alcoholic fermentation. The theoretical ratio is 46/44=1·045, and Pasteur, as quoted above, actually found 51·11 parts of alcohol to 49·42 of carbon dioxide from 100 of cane sugar. He, however, considered that succinic acid and glycerol were formed according to the equation:

$$49C_6H_{12}O_6 + 30H_2O = 12C_4H_6O_4 + 72C_3H_8O_3 + 30CO_2,$$

and therefore ascribed 0·53 of carbon dioxide to the fermentation which had produced 0·67 of succinic acid, thus leaving 48·89 of carbon dioxide as the product of the true alcoholic fermentation, the corrected ratio being thus 51·11/48·89=1·045, exactly the theoretical. Similar results were obtained by Jodlbauer (Zeitsch. Rüb. Zuck. Ind. 1888, 308), who found that cane sugar yielded 49·04 p.c. of carbon dioxide.

Buchner and Meisenheimer (Ber. 1910, 43, 1773), working with pure yeast (Race 792 of the Berlin Collection), obtained 49·73 p.c. of the cane sugar as alcohol, and 49·12 p.c. as carbon dioxide, the ratio being 1·01. They ascribe this excess of carbon dioxide to the oxidation corresponding to the production of glycerol, the amount of which was not estimated. In spite of the fact that no nitrogenous material was added to the medium, the carbon dioxide and alcohol only represent 98·85 parts of the 105·36 of invert sugar to be accounted for, so that 6·51 parts had undergone some other change. Any carbon dioxide formed from amino-acids produced by autolysis would be included in the amount found.

6. *Formation of glycogen: autofermentation of yeast.* Yeast very readily converts a portion of the carbohydrate present in the medium into glycogen $C_6H_{10}O_5$, which is stored in the cell (*see* Harden and Young, Chem. Soc. Trans. 1902, 1224, where the literature is cited).

This material acts as a reserve carbohydrate, and, when the yeast is preserved in absence of sugar solution, is slowly broken down by a diastatic enzyme into sugar, and fermented into alcohol and carbon dioxide: this phenomenon is known as the autofermentation of yeast. As yeast may contain as much as 30–40 p.c. of its dry weight of glycogen, it follows that a very considerable amount of carbon dioxide and alcohol may be produced from yeast alone. The autofermentation proceeds more rapidly at high temperatures (Harden and Rowland, Chem. Soc. Trans. 1901, 1227), and is greatly accelerated by the addition of many salts (Harden and Paine, Chem. Soc. Proc. 1911, 103) and of toluene. The conditions of formation of glycogen have been investigated quantitatively by Pavy and Bywaters (J. Physiol. 1907, 36, 149), and microscopically by Wager and Peniston (Annals of Botany, 1910, 24, 45; J. Inst. Brewing, 1911).

The alcoholic enzyme of yeast. Attention has already been called to the fact that up to 1897 all attempts to isolate from a yeast an enzyme capable of producing alcoholic fermentation had failed. It had early been shown, at first by Mitscherlich (1841) and then by Helmholtz, that the process of fermentation in all probability took place within the cell and the efforts of later investigators had been rightly directed towards the extraction of an enzyme by

some process of disintegration or treatment with solvents. All such efforts were, however, made in vain, as were also attempts to extract the enzyme by freezing or plasmolysis, the products obtained being either inactive or owed what activity they possessed to the presence of unbroken yeast cells or bacteria (Lüdersdorff, Schmidt, Pasteur, Marie von Manassëin, Adolf Mayer, Nägeli, and Loew). A slight modification of the grinding processes which had been used by several of these authors, led, however, to success. Hans and Eduard Buchner applied to yeast the process of grinding with sand which they had previously employed successfully for bacteria. By adding kieselguhr, at the suggestion of Hahn, to the pasty mass obtained, and submitting the mixture to a high pressure, they obtained a clear liquid which was capable of fermenting sugar (Buchner, Ber. 1897, 30, 117).

The nature of the active agent in yeast juice. Buchner at once established the facts that the yeast juice, prepared as just described, was capable in the absence of yeast cells of producing alcoholic fermentation, and that this power was not removed by the addition of chloroform, benzene, or sodium arsenite, by precipitation with alcohol, by evaporation to dryness at 30°–35°, or by filtration through a Berkefeld candle, whereas it was completely destroyed at 50°. He therefore concluded that the fermentative power of the juice was due to a dissolved substance of the nature of an enzyme to which he gave the name of zymase. Several of the properties of this liquid, however, suggested to various investigators that it did not contain an enzyme of the ordinary kind, but rather fragments of the living protoplasm of the yeast, which retained for some time the functions which they had possessed in the cell. This idea was in harmony with the facts that the fermenting power of the juice was rapidly lost on preservation, and that comparatively large amounts of certain antiseptics did undoubtedly greatly diminish its activity. Other objections, founded on the behaviour of the juice on dilution, &c., proved not to be well founded. Further experience of the nature of yeast juice has shown that this idea has little to recommend it. The action of antiseptics is closely analogous to their effect on other enzymes, and the loss of fermenting power has been shown to be a very complex phenomenon. No evidence of the existence in the juice of undissolved protoplasmic fragments has been put forward, and experiments on the precipitation of the juice by alcohol and ether show that if these fragments do exist they are able to withstand repeated solution in water or dilute glycerol and reprecipitation without losing their power of producing fermentation. Such properties are only consistent with the presence of an enzyme, and there seems at present no reason to doubt the existence of such an agent in yeast juice.

Preparation and properties of yeast juice. Fresh brewery yeast is washed and pressed out at about 50 kilos. per sq. cm. The resulting mass, which contains about 70 p.c. of water, is mixed with an equal weight of sand, and from 0·2–0·3 part of kieselguhr, care being taken that this is free from acid. The dry powder thus formed is then ground in small portions at a time in a large porcelain mortar by means of a heavy pestle, until the mass becomes pasty, which occurs after about 1–2 minutes' grinding. The paste is then either directly pressed out after being wrapped in a filter cloth, the pressure being gradually raised to 90 kilos. per sq. cm. (Buchner), or is mixed with more kieselguhr and the dry powder pressed out between layers of chain cloth (MacFadyen, Morris, and Rowland).

The yield of juice obtained from 1000 grams of bottom yeast by Buchner is about 320–460 c.c.; that obtained from English top yeasts is rather smaller, averaging 250 c.c. (Harden and Young). The product, after any suspended yeast cells have been removed by filtration or centrifugalisation, is a slightly viscid, brownish-yellow, opalescent, faintly acid liquid of sp.gr. 1·03–1·06. It contains about 8·5–14 p.c. of dissolved solids, and 0·7–1·7 p.c. of nitrogen, nearly all in the form of albumin, so that the liquid coagulates when heated. The ash amounts to 1·4–2 p.c. and, like that of yeast, contains a large proportion of phosphoric oxide.

When the juice is preserved, the protein becomes hydrolysed owing to the presence of a powerful tryptic enzyme, known as *yeast endotryptase*. At the same time, the power of producing alcoholic fermentation is lost, and it seems probable that this is due to the action of the tryptic enzyme on the alcoholic enzyme (Buchner). When excess of sugar is added and the mixture incubated at 25°, a steady fermentation ensues, carbon dioxide being evolved and alcohol produced in nearly the theoretical ratio, at a rate which gradually decreases until the process stops, after 72–96 hours, not from exhaustion of the sugar, but owing to the destruction of the active agent of fermentation. The juice from bottom yeasts appears to be more stable and to produce a somewhat greater total fermentation than that from top yeasts, 25 c.c. of juice producing on the average at 25° an evolution of about 1–1·5 grams of carbon dioxide in the case of bottom yeast, and 0·5–1 gram in the case of top yeasts.

The juice ferments those sugars which are fermentable by the yeast from which it is prepared and, in addition, dextrin, soluble starch, and glycogen, the first of which is only slowly and imperfectly fermented by yeast, and the last two not at all, as already explained. Maltose and cane sugar are hydrolysed before being fermented, and the fermentation proceeds just as with the simple sugars, glucose, fructose, and mannose. Slight differences between the rates of fermentation and the total fermentations produced with these three sugars, have been observed by Harden and Young. A yeast, which ferments galactose, yields a juice which also ferments this sugar, but the action is often much less pronounced relatively to that on glucose than is that of the living yeast (Harden and Norris).

Yeast juice, like living yeast, exhibits the phenomenon of autofermentation, which is carried out at the expense of the glycogen present in it. A diastatic enzyme, capable of hydrolysing glycogen, exists in the juice (*glycogenase*), and hence added glycogen is also fermented, but usually at a lower rate and with a smaller total yield of gas than glucose. The autofermentation of the juice from top yeast is often very considerable in amount, and may even

occasionally equal that produced with glucose, whilst it is less pronounced with juice from bottom yeast.

The rate of fermentation of sugar varies with the concentration of the sugar in the manner characteristic of enzymes, and in this respect the juice closely resembles living yeast. After a certain small limit of concentration is attained, the initial rate is practically independent of the concentration of the sugar, but decreases slightly as this increases. The gradual destruction of the enzymes produces a gradual fall in rate which simulates the course of a monomolecular reaction, and is regarded by some investigators as evidence that the reaction is of this type (Euler, Zeitsch. physiol. Chem. 1905, 44, 53). Increased concentration of the sugar also increases both the duration of fermentation and the total fermentation, probably owing to a protective action on the fermenting mechanism. The rate of fermentation is diminished by dilution, and, with juice of high fermenting power, is probably proportional to the concentration of the juice. The total fermentation produced is, at the same time, slightly diminished.

Accompanying the decomposition of the sugar into carbon dioxide and alcohol, a synthetic action proceeds, by which a portion of the glucose is converted into a polysaccharide, which is reconverted into glucose by hydrolysis with acid. Hence the observed loss of sugar as estimated by reducing power is usually considerably greater than the sum of the weights of alcohol and carbon dioxide produced. The exact nature of this complex saccharide has not yet been determined, but observations by Cremer (Ber. 1899, 32, 2062) point to the possibility of the synthetic production of glycogen in yeast juice. As already mentioned, succinic acid and fusel oil are not formed by yeast juice, whereas glycerol is produced to the extent of about 3·8 p.c. of the sugar fermented.

The action of antiseptics on yeast juice has been investigated in some detail. Saturation with chloroform or toluene or the addition of 1 p.c. of thymol has practically no effect, whilst the inhibiting action of substances like phenol, formaldehyde, benzoic acid, and salicylic acid, is very small in 0·1 p.c. solution, more considerable in more concentrated solutions. The fermenting power is destroyed by 4 p.c. chloral, 1·2 p.c. phenol, 2 p.c. sodium fluoride, 0·55 p.c. ammonium fluoride, or 1·2 p.c. hydrocyanic acid; but in this last case it is restored when the hydrocyanic acid is removed by a current of air. The action of potassium arsenite is somewhat complex, and is treated later.

Fermentation by dry preparations of yeast and yeast juice. Yeast juice can be evaporated to dryness at 37° without loss of fermenting power as measured by the total fermentation produced. When the juice is brought into 10 volumes of acetone and rapidly drained, washed with ether, and dried, a white powder is obtained, which is almost completely soluble in dilute glycerol, and retains the fermenting power of the original juice. Dry preparations can also be obtained from yeast without any previous grinding, either by drying the yeast in air and then heating it to 100° for 6 hours (*hefanol*) or by treating it twice with a large volume of acetone (or alcohol and ether), washing with ether and drying. The material prepared in the latter way amounts to about 30 p.c. of the pressed yeast taken, and is known as acetone yeast, permanent yeast (*Dauer-hefe*) or zymin, and is almost anhydrous, and quite incapable of growth, but readily produces alcoholic fermentation when brought into sugar solution. The general phenomena of fermentation by its means are the same as are produced by yeast juice. Both the total fermentation and the rate of fermentation are 4–6 times greater than would be obtained with the yeast juice prepared from the same weight of yeast.

The conditions of action of the fermenting agent contained in yeast juice. The investigation of the mode of action of yeast juice on sugar has shown that the process is very complex. The enzyme is accompanied by another substance, termed the *coenzyme*, the presence of which is essential for the production of fermentation, and, moreover, the chemical change is not a simple decomposition of sugar, according to Gay-Lussac's equation, but a complicated reaction in which a salt of phosphoric acid takes part (Harden and Young, Proc. Roy. Soc. B. 1906, 77, 405, 78, 369; 1908, 80, 299; 1909, 81, 336; 1910, 82, 321).

The coenzyme of yeast juice. When yeast juice is passed under pressure through a Martin filter, which consists of a Chamberland filtering candle impregnated with 7–10 p.c. gelatin, all the colloidal matter of the juice is retained on the filter, whilst the dialysable substances pass through, so that the constituents of the juice are divided into two parts. When these two portions, the residue and the filtrate, are separately incubated with sugar solution, it is found that neither of them is capable of producing fermentation. When, however, the two solutions are mixed, fermentation proceeds at almost the same rate as with the original yeast juice (Harden and Young). Yeast juice, therefore, contains a dialysable substance essential for the process of fermentation, and this is provisionally termed the *coenzyme* or *co-ferment*. It is also present in zymin, from which it can be readily removed by simple washing with water, a perfectly inactive residue being left.

The chemical nature of this substance and its exact function in alcoholic fermentation are unknown, and our present information with regard to it may be summarised as follows: (1) The coenzyme is thermostable, and is not destroyed when its solution is boiled. It is therefore present in the liquids obtained by boiling yeast juice and filtering, by heating yeast at 100°, or by boiling zymin with water and filtering, and is best prepared by one of these methods. (2) It is dialysable, and can be removed from yeast juice by dialysis against water (Buchner and Antoni, Zeitsch. physiol. Chem. 1905, 46, 136) as well as by the filtration methods already described. (3) It is destroyed by hydrolysis by acids or alkalis, and even by the continued boiling of its solution. (4) It is gradually destroyed in yeast juice, less rapidly in presence of sugar, by an enzyme, which appears to belong to the group of lipases, since the destruction proceeds more rapidly in the presence of the lipase of castor-oil seeds, but is not accelerated by trypsin (Buchner and Klatte,

Biochem. Zeitsch. 1908, 8, 520). This indicates that the coenzyme probably has the structure of a fat or lipoid substance. (5) It is not precipitated or destroyed by lead acetate, and can therefore be, to some extent, purified by means of this reagent (Harden and Young). It is precipitated by a large volume of acetone or alcohol along with the enzyme and also by colloidal ferric hydroxide (Resenscheck, Biochem. Zeitsch. 1908, 15, 11).

The function of phosphates in alcoholic fermentation. The addition of a soluble phosphate to a fermenting mixture of yeast juice and sugar produces a remarkable effect. The rate of fermentation is greatly increased, and remains at this high value for a certain time, after which it rapidly falls until it is again approximately the same as before the addition of phosphate. During this period of enhanced fermentation, the amounts of carbon dioxide and alcohol produced exceed those which would have been formed in the absence of added phosphate by an amount exactly equivalent to the phosphate added in the ratio $R_2HPO_4 : CO_2+C_2H_6O$ (Harden and Young, Chem. Soc. Proc. 1905, 21, 189). The phosphate is, at the same time, converted into a phospho-organic compound, termed a *hexosephosphate*, of the formula $C_6H_{10}O_4(PO_4R_2)_2$, which is not precipitated by magnesium citrate mixture or uranium salts (Harden and Young; Iwanoff, Zeitsch. physiol. Chem. 1907, 50, 281). In other words, a definite chemical reaction occurs according to the following equation, which is founded on the ratio both of sugar and phosphate to carbon dioxide and alcohol, and on the composition of the hexosephosphate produced:

(1) $2C_6H_{12}O_6+2R_2HPO_4 = 2CO_2+2C_2H_6O+2H_2O+C_6H_{10}O_4(PO_4R_2)_2.$

The existence of this reaction renders it probable that phosphates are essential for the alcoholic fermentation of the sugars by yeast juice, and that in their absence no fermentation can occur. This conclusion has been confirmed in a very striking manner by experiment. By making use of the methods described under the heading of the coenzyme, a mixture of enzyme, coenzyme, and sugar can be prepared which contains no free phosphate or hexosephosphate and very little phosphorus in any form which can yield phosphate by enzymic action. Such a mixture is almost completely devoid of fermenting power, but ferments readily when a small proportion of phosphate is added. In a particular case, the phosphate free mixture only gave 1·5 c.c. of carbon dioxide, whereas in presence of phosphate 132 c.c. were produced (Harden and Young, Proc. Roy. Soc. B. 1911, 83, 451). As the result of the reaction expressed by equation (1), practically the whole of the free phosphate of the juice is converted into hexosephosphate, and the fermentation should therefore come to a close unless some means of regeneration of free phosphate were provided. Actually the necessary phosphate is supplied by the hydrolysis of the hexosephosphate, which is effected by an enzyme, termed on this account *hexosephosphatase*, and yields a hexose and a phosphate:

(2) $C_6H_{10}O_4(PO_4R_2)_2+2H_2O = C_6H_{12}O_6+2R_2HPO_4.$

Both the hexose and the phosphate thus formed enter again into reaction (1). The phosphate thus goes through a regular cycle of changes, being first converted into hexosephosphate and then liberated by hydrolysis.

It is now possible to understand the conditions which prevail in yeast juice in the presence and absence of added phosphate. When the proper or optimum amount of phosphate is added, reaction (1) proceeds at its maximum rate, and this rate affords a measure of the concentration of the fermenting complex present in the juice. When all the phosphate has been converted into hexosephosphate, the rate falls to a low level, which represents the rate at which phosphate is being supplied by the hydrolysis of the hexosephosphate. The rate of fermentation under these conditions, the so-called normal rate of fermentation, is therefore a measure of the concentration of the hexosephosphatase. If it were possible to accelerate the rate of action of this enzyme to such an extent that the supply of phosphate was maintained at the optimum amount, the rate of fermentation would be permanently maintained at the high level observed in presence of added phosphate. Precisely this result is attained by the addition of a small amount of sodium arsenate to the juice. A large and permanent rise of rate occurs, and direct experiment shows that this is due to acceleration of the rate of action of the hexosephosphatase. Arsenites produce a somewhat similar but much less marked effect (Harden and Young, *l.c.*).

Hexosephosphoric acid. The phospho-organic compound produced during fermentation, which was first observed by Harden and Young, has since been studied by Iwanoff (*l.c.* and Cent. Bakt. Par. ii. 1909, 24, 1); Lebedew (Biochem. Zeitsch. 1909, 20, 114; 1910, 28, 213) and Young (Proc. Roy. Soc. B, 1909, 81, 528; Biochem. Zeitsch. 1911, 32, 177). It is isolated in the form of the lead salt from the boiled mixture in which fermentation has been carried out in presence of phosphate. This is decomposed by sulphuretted hydrogen, neutralised, the free phosphate removed by magnesium nitrate and alkali, and the hexosephosphate again precipitated by lead acetate. All the salts are amorphous, and the magnesium, calcium, barium, and manganese salts, which are only sparingly soluble, are more soluble in cold than in hot water, and can be purified by taking advantage of this property. The free acid has not been obtained in the pure state. It is decomposed when boiled alone or with acids yielding phosphoric acid and either pure fructose or a mixture of hexoses in which fructose predominates. Glucose, mannose, and fructose all appear to yield the same hexosephosphoric acid, which gives fructose when hydrolysed.

Some doubt exists as to the constitution of this compound. Iwanoff regards it as a triosemonophosphoric acid ester $C_3H_5O_3(PO_4H_2)$, but the evidence on which this view rests has been shown to be unsatisfactory. Lebedew, on the other hand, considers that it is a hexosemonophosphoric acid ester, basing this view solely on the composition of the phenylhydrazine derivative, which has the composition $C_6H_5NH{\cdot}NH_2,H_2PO_4CH_2[CH{\cdot}OH]_3C(N_2C_6H_5)CH(N_2C_6H_5)$ and is therefore the *phenylhydrazine salt of a monophosphoric ester of hexosazone*. Young,

however, supports the original view of Harden and Young, which is now accepted by Lebedew, that the compound is a hexosediphosphoric ester $C_6H_{10}O_4(PO_4H_2)_2$, since analyses of the salts agree with this formula; phosphoric acid is split off during the formation of the phenylhydrazine derivative, and a *hydrazone* containing two phosphoric acid groups for one molecule of hexose has been prepared.

Hexosephosphates are present in freshly prepared yeast juice and in yeast extract, and are therefore almost certainly present in the living yeast cell.

Several minor points remain for consideration with regard to the action of phosphate. In the first place, phosphate not only sets up a temporarily enhanced fermentation, but also considerably increases the total fermentation produced, apparently by means of a protective action of the hexosephosphate on the various enzymes concerned. Excess of phosphate produces a secondary inhibiting effect, and may lead to a diminished fermentation instead of an enhanced fermentation. Excess of arsenate and arsenite produce similar effects but are much more marked in their action, often leading to total inhibition. The nature of the action which leads to this result is not yet known.

Fructose produces a much greater rate of fermentation in presence of phosphate than does glucose, and the optimum concentration of phosphate is greater in presence of fructose than in presence of glucose, as shown by the following numbers referring to 10 c.c. of yeast juice :—

Optimum concentration of phosphate in terms of a molar solution		Maximum rate of fermentation in c.c. of CO_2 per 5 minutes	
Glucose	Fructose	Glucose	Fructose
0·034	0·085	7·5	32·2
0·012	0·120	5·4	28·4
0·026	0·130	8·0	17·0
0·120	0·180	16·2	31·2

These facts are, at present, not understood, but they probably indicate that fructose bears some special relation to the fermenting complex.

Zymin also reacts with phosphate in a similar manner to yeast juice, but the rate is not so greatly increased, so that the effects are not so marked.

The play of enzymes in yeast juice. It will be seen from the foregoing that the number of factors concerned in fermentation by yeast juice is very large, and that the conditions are correspondingly complex. In addition to the enzyme and coenzyme, together forming the fermenting complex, the hydrolytic enzyme hexosephosphatase, the free phosphate and the sugar, which are all directly involved in fermentation, a number of other agencies are at work which influence the course of the reaction. Chief among these are the hydrolytic enzymes which cause the destruction of the enzyme and coenzyme respectively. The former of these is probably proteoclastic and the latter lipoclastic, and on the relative concentration of these and of the enzyme and coenzyme themselves depends the exact course of events. During the normal fermentation in presence of excess of sugar, both the enzyme and coenzyme are gradually being destroyed, and fermentation ceases as soon as either of these has completely disappeared. In juice from top yeast, it is found that the cessation of fermentation is due to the disappearance of the enzyme. Buchner and Klatte (Biochem. Zeitsch. 1908, 8, 520) have, however, found that in juice from bottom yeast the coenzyme disappears first, and that the fermentation can be restarted by the addition of boiled yeast juice containing a fresh supply of coenzyme. The matter is even more complex than this, for boiled yeast juice has been found to contain an antiprotease (analogous to the antitrypsin of blood serum) which inhibits the action of the trypsin of the yeast, and thus preserves the enzyme from destruction. The presence of this agent is partly responsible for the considerable increase in total fermentation produced by the addition of boiled yeast juice to fresh yeast juice, the coenzyme and the phosphate added at the same time having also a share in the phenomenon. The hexosephosphatase appears always to outlast both the enzyme and coenzyme. The addition of sugar alone also exerts a protective action upon the enzymes of the juice, the power of producing fermentation being retained for a much longer time in presence than in absence of the sugar. All these phenomena of protection are probably to be referred to the formation of some sort of compound or association between the substances concerned in fermentation, which renders them less capable of reaction with other substances.

The nature of the process of fermentation in the living yeast cell. When the effects produced by yeast juice and zymin are compared with those due to living yeast, it is found that yeast juice ferments glucose at a rate which is only about $\frac{1}{10}$ of that given by the yeast from which it was prepared, whilst zymin yields a rate which is $\frac{1}{7}$–$\frac{1}{15}$ of that of yeast. In the presence of fructose and phosphate, the rate of fermentation of yeast juice may be increased as much as 20-fold, then amounting to about one-half the rate of that of living yeast, whilst that of zymin may be increased to approximately the same relative value. Assuming, as appears justified, that the process of fermentation is of the same general character in yeast as in yeast juice, it follows that yeast juice contains a large fraction of the fermenting complex present in yeast, but differs from this mainly in the power of regenerating phosphate. Zymin appears to contain a somewhat smaller proportion of the fermenting complex, but has a much greater power of regenerating phosphate than yeast juice, although still considerably less than living yeast. A similar effect to that which is produced by grinding yeast, treating it with acetone or drying and heating it, is also produced, but to a smaller degree, by treating it with toluene (Harden), so that all these processes must result in some similar change which is rendered evident by the loss of the power of regenerating phosphate from hexosephosphate. Of the nature of this change we are, at present, ignorant, but the facts strongly suggest that it is in some way due to the disorganisation of the cell. Another difference between yeast juice and yeast is that the latter does not respond, like yeast juice, to the addition of phosphate or of arsenate. This is in reality another consequence of the superior phosphate producing power of the yeast cell, whereby the optimum amount of phosphate is constantly supplied.

In the light of what has been said, the following scheme of fermentation in the yeast cell may be imagined. The sugar first diffuses into the cell, and it has been shown by Slator and Sands that the rate of diffusion is much more than sufficient to supply the sugar necessary for fermentation, and is therefore not the controlling factor in the observed rate of fermentation (Chem. Soc. Trans. 1910, 922). Inside the cell, the sugar, either as such or having undergone some change such as conversion into the enolic form (E. F. Armstrong), combines with the fermenting complex, and is thereby brought into relation with phosphate, probably also combined with the fermenting complex. This association of fermenting complex, sugar, and phosphate then breaks down with liberation of the fermenting complex, accompanied either by the formation of carbon dioxide, alcohol, and hexosephosphate, according to equation (1) previously given, or of the products of some intermediate stage of this reaction. It is probably the rate of this decomposition which is measured as the rate of fermentation. The hexosephosphate is rapidly hydrolysed and a supply of fresh phosphate thus provided, which, along with the hexose formed at the same time, and a new quantity of sugar supplied by diffusion, again enters into association with the fermenting complex, and thus continues the fermentation.

The results obtained by Slator with mannose and the facts already related with regard to galactose, suggest the possibility that the whole mechanism, or at least some portion of it, may be specific for each sugar, but definite evidence of this has not yet been obtained.

The chemical changes involved in alcoholic fermentation. Many theories have been advanced as to the stages which may be supposed to intervene between glucose and the final products of its decomposition—alcohol and carbon dioxide. Baeyer, in 1870, pointed out that the alternate removal and readdition of the elements of water might lead to an accumulation of oxygen on certain of the carbon atoms, and thus render the rupture of the carbon chain possible. Wohl has proposed a modification of this idea, which leads to the supposition that loss of water and intramolecular change result in the formation of a ketoaldehyde which undergoes hydrolysis to methylglyoxal and glyceraldehyde; the latter of which, by a similar series of changes, also forms methylglyoxal $CH_3 \cdot CO \cdot CHO$. This then passes into lactic acid, and this into carbon dioxide and alcohol. This theory received a certain amount of experimental support from the fact that small quantities of lactic acid appear to be fermented by yeast juice (Buchner and Meisenheimer). The occurrence of lactic acid as a true intermediate product of alcoholic fermentation has, however, now been abandoned, largely owing to the criticisms of Slator, who pointed out that this substance should be fermented at least as quickly as glucose, and that this is not the case. The same criticism is valid against all the various 3-carbon compounds which have been proposed as intermediate products, including glyceraldehyde and dihydroxyacetone, both of which are, according to Buchner and Meisenheimer, slowly attacked by yeast, whilst dihydroxyacetone is also readily fermented by yeast juice prepared by maceration (Lebedew).

Much further evidence is required before any satisfactory conclusion can be arrived at with regard to this subject, and the facts must certainly be taken into account that two molecules of sugar are involved in the reaction, and that the products include hexosephosphate as well as alcohol and carbon dioxide.

Fermentations produced by Bacteria.

Bacteria are capable of bringing about many fermentations which are strictly analogous to the fermentation of the sugars by yeast. Many species of bacteria are, however, much less restricted in their power of action, and decompose not only the simple hexoses and complex saccharides, but also the glucosides, the lower sugars, especially the pentoses, and the corresponding alcohols including glycerol, as well as many organic acids. In addition to this, they also act upon nitrogenous compounds, and effect many oxidations and reductions. The chemical changes involved are of the most varied kind, and although they are in all probability brought about by enzymes, it is only in comparatively simple cases that the enzyme has been separated from the cell. In some cases, however, the enzymes pass into the surrounding medium, this being frequently the case with the various digestive enzymes, and possibly with the urease which brings about the hydrolysis of urea into ammonium carbonate and water.

Interesting and important attempts have been made by Buchner to prepare extracts containing active enzymes from the bacteria of the lactic acid and acetic acid fermentations, by a process similar to that employed for yeast, but in both cases without success. He was able, however, to demonstrate the existence of such an enzyme in the cell by treating the organism with acetone, and showing that the dead and sterile material was still capable of converting sugar into lactic acid in the one case, and of oxidising alcohol to acetic acid in the other.

Although the qualitative characteristics of the action of bacteria on many substances are well known and are largely used for purposes of identification and differentiation, comparatively little strictly quantitative work on the subject has been done, in which all the products derived from a known weight of a material have been estimated, and hence our knowledge of the chemistry of bacterial action remains very imperfect. Among the pioneers in this branch of the subject must be reckoned Fitz (who, however, often employed mixed cultures) and P. F. Frankland. The employment of mixed cultures is not entirely without justification, since many of the changes produced in nature by bacteria, such as putrefaction, are brought about by the combined or successive action of different organisms, some of which make use of the products of decomposition formed by others.

The chief types of fermentation produced by bacteria may be classified in much the same manner as those due to enzyme action, under the heads of (1) hydrolysis; (2) decomposition involving the rupture of a carbon chain; (3) oxidation; (4) reduction and deoxidation.

I. Fermentations by Hydrolysis.

A large number of bacteria contain enzymes, which enable them to bring about processes of hydrolysis, whether of proteins or carbohydrates, and in some cases these are soluble and pass into the medium.

(*a*) **Liquefaction of gelatin.** Proteoclastic enzymes capable of liquefying gelatin are almost certainly present in all bacteria, but they are only excreted by certain organisms, and therefore afford a differential test often employed as an aid in identification. For this purpose, the organism is grown on nutrient gelatin, and note is taken as to whether the gelatin becomes liquefied. Prominent among the organisms which liquefy gelatin in this way are *B. fluorescens liquefaciens* (Flügge), *B. vulgaris* (Lehm. and Neum.), &c., whilst the intestinal organisms of the *B. coli* group are non-liquefiers. The liquefaction of gelatin is the first step in the hydrolysis of this substance, and is often followed by a more deep-seated decomposition of the resulting simpler compounds, which is discussed later on under the heading of *Putrefaction*. Some organisms only bring about the liquefaction of gelatin when grown in air, but do not liquefy in it an atmosphere of hydrogen or nitrogen, although growth takes place.

(*b*) **Hydrolysis of polysaccharides and glucosides.** It seems probable that most bacteria resemble yeasts in the fact that, when brought into contact with polysaccharides, they do not ferment them directly, but first hydrolyse them and then ferment the resulting simple sugars; and the same thing is true of the glucosides. In most cases no strict proof of this has been brought, but in some the hydrolysis has been actually demonstrated. Thus Bertrand and Weisweiller (Ann. Inst. Past. 1906, 20, 977) found that the *B. bulgaricus* (Grig.) hydrolysed milk sugar before producing lactic acid from it, and were able to prove the existence of glucose and galactose in the partially fermented solution. The determination of the fermentability or non-fermentability of the di- and tri-saccharides, starch, dextrin, inulin, and many glucosides, is now largely employed for the identification of bacteria, especially those of the *B. coli* group and the *Streptoccoci*. It follows from the foregoing that what is being tested for in such cases is most probably the presence or absence of the ferment requisite for the hydrolysis in question, *e.g.* invertase by cane sugar, maltase by maltose, lactase by lactose, β-glucosidase by many glucosides, such as saligenin, amygdalin, &c.

The presence of the hydrolytic ferment is rendered evident by the subsequent fermentation of the resulting simple sugars, &c., with production of acid or evolution of gas or both. The efficacy of the test, therefore, depends on the ability of the organism to ferment at least one of the products of the hydrolysis.

(*c*) **The ammoniacal fermentation of urea.** The waste nitrogen of the animal body is excreted in the urine, chiefly in the form of urea $CO(NH_2)_2$, uric acid $C_5H_4O_3N_4$, and hippuric acid $C_6H_5{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}COOH$. In the urine of man, about 30 grams of urea are passed per diem, along with 0·7 gram of uric acid, and very small amounts of hippuric acid; whilst the urine of graminivorous animals contains comparatively large amounts of urea and hippuric acid (Liebig, 1829), the urine of a cow containing 18 grams of urea and 16 of hippuric acid per litre. On the other hand, the nitrogenous waste of birds and snakes is excreted almost entirely in the form of uric acid. The conversion of the nitrogen of these substances in the soil back into ammonia, which is then rendered available for plants by nitrifying organisms, is of vast importance, as it is in this way that the nitrogen balance of the soil is maintained, practically the whole nitrogen of natural manures being present in these forms.

When urine, which is normally sterile and acid in reaction, is exposed to air, it becomes alkaline, the urea being converted into ammonium carbonate:

$$CO(NH_2)_2+2H_2O=(NH_4)_2CO_3.$$

This change was observed at a very early date, and was ascribed by Liebig, in accordance with his theory of fermentation, to the presence of decomposing mucus from the bladder. About 1860, however, it was established by Pasteur (Compt. rend. 1860, 50, 849), his pupil, van Tieghem (*ibid.* 1861, 52, 210; 1864, 58, 210), and Müller (J. pr. Chem. 1860, 81, 452), that the decomposition was produced by a micrococcus which was termed *Torule ammoniacale* by Pasteur, and later *Micrococcus ureæ* by Cohn. It has since been found, as the result of numerous researches by Flügge, Heræus, Warington, Leube, Beyerinck, and especially Miquel (literature quoted in article by Miquel in Lafar, Technische Mykologie, iii. 71), that a large number of organisms have the power of producing this change. More than thirty varieties have been described by Miquel alone, who has also found that these organisms occur freely in water, air, and soil, the cocci being about twice as frequent as the bacilli, whilst 1–2 p.c. of the organisms of the Paris water, air, and cultivated soil belong to this class. The most characteristic and commonly occurring coccus is that originally discovered by Pasteur, now known as *Urococcus van Tieghemi* (Miquel), which is a small diplococcus, and grows well on ordinary media, not liquefying gelatin. In presence of urea, the growth on solid media becomes surrounded by dumb-bell-shaped crystals, which are insoluble in water, and consist of the phosphates and carbonates of calcium, precipitated from the medium by the ammonia produced. This is a very characteristic phenomenon, and renders it easy to detect not only this organism but any urea ferment among a number of organisms which do not attack urea. The organism readily decomposes as much as 4–4·5 p.c. of urea in the medium, but is very susceptible to antiseptics.

The most energetic decomposition of urea is brought about by the *Urobacillus Pasteurii* (Miquel) isolated from sewage. This is a motile, sporing bacillus, which grows well in alkaline broth, which it renders viscid and ropy. It ferments completely as much as 13 p.c. of urea in the medium, and has been observed to decompose 3·3 grams of urea per hour per litre of culture.

As early as 1876, Musculus (Compt. rend. 1874, 78, 132; 1876, 83, 333) found that the slimy urine of patients suffering from cystitis,

and probably infected by the foregoing urobacillus, contained a soluble ferment which could be precipitated by alcohol and was capable of converting urea into ammonium carbonate in the absence of bacteria. Pasteur and Joubert, on the other hand, maintained that this action was due to the presence of an organism (Compt. rend. 1876, 83, 1).

The question of the existence and properties of this enzyme has been studied by many investigators (Leube, Lea, Beyerinck, Miquel, Moll) with somewhat discrepant results, ascribed by some to the unstable character of the enzyme. It can hardly, however, be considered as definitely proved that the enzyme has been obtained free from bacteria. According to Miquel, it can readily be obtained in solution by inoculating alkaline beef broth containing urea with one of the urea-fermenting organisms, and, after some time, filtering through a biscuit porcelain candle. The liquid is then sterile and capable of decomposing as much as 100–120 grams of urea per litre per hour at 48°. Its activity is greatly increased by cane sugar and glycerol, and is very readily inhibited by antiseptics. It may be precipitated by the addition of 2 volumes of alcohol. Musculus employed a turmeric paper moistened with a solution of the enzyme as a test for urea, the liberated ammonia producing a brown colour, and Miquel has proposed the use of solutions of the enzyme for the quantitative estimation of urea as ammonia. A very powerful urease exists in the soya bean.

(*d*) **The fermentation of uric acid.** Uric acid readily undergoes a combined bacterial oxidation and hydrolysis, but little is known as to the nature of the bacteria which produce the change (Sestini, Gazz. chim. ital. 1889; Gérard, Compt. rend. 1896, 122, 1019; 123, 185; Ulpiani, Atti Lincei, 1903, 12, 236). It seems probable that urea is first produced and then further hydrolysed:

$$C_5H_4O_3N_4+2H_2O+3O=2CO(NH_2)_2+3CO_2.$$

(*e*) **The fermentation of hippuric acid.** Van Tieghem (Compt. rend. 1864, 58, 210) showed that the same micrococcus which fermented urea also effected the hydrolysis of hippuric acid into benzoic acid and aminoacetic acid, into which it is also converted by acids:

$$C_6H_5CO\cdot NH\cdot CH_2\cdot COOH+H_2O = C_6H_5\cdot COOH+NH_2\cdot CH_2\cdot COOH.$$

It has since been found that more than one of the urea-fermenting organisms produce this change (Rattone and Valenta, Arch. Scienz. mediche, 1886, 10, 311). In the soil, the aminoacetic acid then probably undergoes one of the characteristic changes described under *Putrefaction*, its nitrogen being liberated as ammonia.

2. Fermentations by Decomposition accompanied by the Rupture of a Carbon Chain.

The chief chemical characteristic of this form of fermentation is that it involves the rupture of the carbon chain of the fermentable substance, the products being, as a rule, substances containing a smaller number of carbon atoms than the original compound. In many cases, however, a secondary synthesis occurs, and compounds are then found among the products containing more carbon atoms in the molecule than the original substance, the best known example of this being the production of butyric acid from glycerol.

As regards the nature of the changes produced, the same intramolecular oxidation and reduction is observed as characterises the alcoholic fermentation of sugar. Carbon dioxide is very frequently evolved, and this is often accompanied by free hydrogen, less frequently by marsh gas. The hydrogen thus formed is capable of bringing about the reduction of many substances such as nitrates, amino-acids, &c., which may be present in the medium, and thus modifying the result. In many cases in which no gas is evolved, formic acid is produced in considerable quantity, and this substance is sometimes found in comparatively small amount, even when carbon dioxide and free hydrogen have been evolved. The production of ethyl alcohol is also a feature of common occurrence, and methyl, propyl, and *iso*propyl alcohols have all been observed as well as acetone, acetylmethylcarbinol, and butyleneglycol. Among the other products, lactic acid, which has the same empirical formula as glucose, is one of the most frequent. In some cases, the conversion of a sugar into lactic acid is almost quantitative, whilst in others this acid forms only a small proportion of the whole product. Acetic acid, which also has the same empirical formula as glucose, is also a common product, and is sometimes accompanied by propionic and other of the fatty acids. Characteristic of one type of fermentation is the production of butyric acid, accompanied by more or less butyl alcohol. An almost invariable product of the bacterial fermentation of sugars and alcohols is succinic acid, probably in part derived, as in alcoholic fermentation, from the decomposition of amino-acids.

Although bacteria are much less specific in their power of fermentation than the yeasts, they nevertheless display great sensitiveness to small changes in chemical composition and configuration. Thus many organisms are known which attack mannitol, but not the stereoisomeric dulcitol, and similar relations are not uncommon.

Since a single species of bacterium may attack a very large number of different compounds, and the same compound may be decomposed in several distinct ways by different organisms, no very satisfactory classification of these fermentations can be effected, and they are best grouped according to the most characteristic of the products.

They will be briefly summarised here under the following heads:—

(*a*) **The true lactic fermentation.** In this decomposition, lactic acid is almost the sole product, the change proceeding practically in accordance with the equation:

$$C_6H_{12}O_6=2C_3H_6O_3.$$

The spontaneous souring and clotting of milk have long been known to be due to the production of lactic acid, which causes the precipitation of the caseinogen. The process was at first ascribed to the action of the caseinogen itself, which was regarded as an enzyme (Bouitron; Charlard and Fremy). The souring of milk, even after it had been heated and protected from the access of air-borne germs (due to the presence of sporing bacilli), played a part

of some importance in the history of the development of the theory of fermentation, and was cited by the supporters of Liebig's view, that fermentation was not due to living organisms (Gerhardt). The existence of a lactic acid producing organism was first definitely established by Pasteur (Compt. rend. 1857, 45, 813; 1858, 47, 224; Ann. Chim. Phys. 1858, [3] 52, 404), and was confirmed by Lister, in 1877, who succeeded in preparing a pure culture of an organism capable of souring milk by diluting soured milk to such an extent that a drop only contained a single organism, adding a single drop of this to sterile milk, and repeating the process several times. Since then the question has been the subject of an enormous number of investigations on account of its technical importance (*see* Lafar, Technische Mykologie, vol. 2; Henneberg, Gärungsbakteriologisches Praktikum, Berlin, 1909), and only a few of the most interesting results can be mentioned here.

It has been found that all liquids containing saccharine matter are liable to become sour, owing to the production of lactic acid, when they are exposed to the air. The organisms capable of producing this change are extremely numerous, and the nature of the flora developed in any particular case depends on the kind of sugar present and the character of the nitrogenous nutriment available. Thus the lactic acid organism of milk is capable of fermenting milk sugar, whilst that of beer cannot attack this substance. The chief lactic acid organisms have been isolated from milk, beer, distiller's mash, baker's yeast, dough, sauerkraut, and similar materials. They are all non-motile, and do not form spores.

Lactic acid is manufactured by the action of a bacillus on various saccharine solutions prepared from barley, maize, potatos, &c., the starch being first hydrolysed by acid or malt, and the fermentation carried on in the presence of chalk. The organism chiefly employed for this purpose is the *B. Delbrücki* (Leichmann) identical with the *B. longissimus* (Lafar), which forms long cells (3–7μ) and grows well at 46°–47° in unhopped wort, distiller's mash, and yeast water, but not in milk or beer. It converts glucose, cane sugar, and maltose into lactic acid, and produces neither volatile acids nor alcohol. This bacillus also occurs in the unsterilised mash employed by distillers, where it is allowed to grow in order to render the liquid sufficiently acid to prevent subsequent infection by harmful bacteria during the fermentation by yeast.

A second important organism of this class is the *Saccharobacillus pastorianus* (van Laer), which frequently invades beer wort and renders the beer sour. A closely allied variety is employed in the manufacture of the Berlin white beer to impart a certain desired degree of acidity. This organism, however, produces small amounts of alcohol, acetic acid, and formic acid. It forms long cells often united to tangled threads.

The souring of milk is a very complex phenomenon, in which many bacteria belonging to different types take part, the predominant organism varying with the temperature at which the milk is preserved. The most commonly occurring organism appears to be the *Streptococcus lacticus* (Kruse), formerly known as *Bact. Güntheri* (Lehmann and Neumann), *B. lactis acidi* (Kruse), *B. acidi paralactici* (Kozai). This organism, of which there appear to be many races or varieties, forms round or oval cells, grows very feebly on nutrient gelatin, and is positive to Gram's staining reaction. It converts glucose almost completely into *d*-lactic acid, traces of volatile acids being also formed. Thus Weigmann (Jahrsb. Molk. Kiel, 1890–91, 25; 1891–92, 24), and Leichmann (Milchzeit. 1896, 25, 67) have found that in milk the lactic acid produced amounts to 89–98 p.c. of that calculated for the complete conversion of the milk sugar fermented into this substance.

Another organism, which has attained a certain degree of notoriety from its use for the preparation of sour milk as an article of diet, was found by Massol in Yoghurt, a sour milk used as food in Bulgaria. It is known as *B. bulgaricus* (Grigoroff), and forms long cells which grow feebly on agar, forming tangled masses of delicate threads. Its action on milk has been very thoroughly investigated by Bertrand and Weisweiller (Ann. Inst. Past. 1906, 20, 977). It has practically no action on the fat, and only hydrolyses a very small proportion of the caseinogen. On the other hand, it hydrolyses the milk sugar almost completely, and ferments the resulting galactose and glucose, forming lactic acid, containing an excess of the *d*-acid, and amounting to about 92 p.c. of the hexoses fermented, about 2 p.c. each of acetic and succinic acids, traces of formic acid, and no alcohol.

The *B. acidi lactici* of Hueppe, which was at one time thought to be the chief organism concerned in the souring of milk, is not of such common occurrence as was formerly believed, and is more closely related to the following group of organisms than to the true lactic acid bacilli.

(*b*) **The modified lactic fermentation**, in which lactic acid is always accompanied by a considerable proportion of other substances.

Under this head may be classed, along with others, the changes produced in carbohydrates and alcohols by the very varied and complex group of intestinal bacteria, of which *B. coli communis*, *B. typhi*, &c., are well-known representatives. This group of organisms has received a very large amount of attention from bacteriologists for several reasons. In the first place, the group includes a large number of pathogenic organisms, the detection of which is of the utmost importance. In the second place, owing to the universal and abundant occurrence of *B. coli communis* and allied organisms in the intestine, from which they pass into sewage, the presence of these organisms in water intended for consumption is regarded as a sign of pollution by sewage, and the examination for the presence of such organisms is part of the routine of a bacteriological examination of water. For these reasons, the chemical bacteriology of this group has been closely studied, especially on its qualitative side. These organisms possess the common characteristic of growing well at 37°–40°, aërobically in presence of bile salts (the sodium salts of taurocholic and glycocholic acids), and are thus differentiated from a great number of the commoner organisms of air, water, and soil, the growth of which is inhibited by these salts. In

addition to this, almost without exception they decompose glucose with production of acid, or acid and gas. The further chemical differentiation of these organisms depends on their behaviour to the various simple sugars and alcohols, such as the pentoses, hexoses, methylpentoses, glycerol, pentitols, and hexitols and to the complex saccharides and glucosides, to which reference has already been made.

They are all non-sporing bacilli, which either do not liquefy gelatin at all or do so very slowly, are facultative anaërobes, and are negative to Gram's staining test.

They can be distinguished independently of their chemical action by their physiological effects, notably by the agglutination test of Widal. This depends on the fact that each species, and even variety, of organism, when injected into a living animal, gives rise, in the blood serum of that animal, to a substance usually highly specific, termed an agglutinine, which is able to cause clumping and aggregation of the living bacteria when added even in very dilute solution (1 in 10,000–100,000) to a suspension of the organisms. This method affords a very valuable check on the chemical reactions, and its use has shown that in the main these reactions are reliable as a means of identification, although very considerable variations can undoubtedly be produced in the chemical reactions by artificial means, and very probably occasionally occur in nature.

Organism	Glucose	Lactose	Cane sugar	Mannitol	Dulcitol	Arabinose	Indole	V. & P.
B. lactis aërogenes (Esch.)	AG	AG	AG	AG	–	AG	–	+
B. acidi lactici (Hüppe)	AG	AG	–	AG	–	AG	+	–
B. coli communis (Esch.)	AG	AG	–	AG	AG	AG	+	–
B. Neapolitanus (Emmerich)	AG	AG	AG	AG	AG	AG	+	–
B. coscoroba (Tretrop)	AG	AG	AG	AG	–	AG	+	–
B. enteritidis (Gärtner)	AG	–	–	AG	AG	AG	–	–
B. cloacæ (Jordan)	AG	AG	AG	AG	–	AG	–	+
B. typhi (Eberth)	A	–	–	A	–	–	–	–
B. dysenteriæ (Shiga)	A	–	–	–	–	–	–	–
B. pyogenes fœtidus (Passet)	A	A	A	A	A	A	+	–

The above table shows the qualitative reactions of a few of the best-defined of these organisms; AG meaning acid and gas; A, acid only; and – no change. For the sake of completeness, the production of indole from proteins (*see Putrefaction*) is included, as well as Voges and Proskauer's test for the production of acetylmethylcarbinol (a pink colour and green fluorescence when caustic soda is added to a cultivation of the organism in glucose broth), as these are, at present, considered to be valuable tests.

The nature of the action of certain of these organisms on the carbohydrates and higher alcohols has been examined by many authors from various points of view, particularly as regards the nature of the lactic acid formed under various conditions (Péré, Ann. Inst. Past. 1893, 7, 737; 1898, 12, 63), the nature of the gas evolved (Theobald Smith, Cent. Bakt. Par. 1895, 18, 1; *see* Keyes, J. Medical Research, 1909, 21, 69, where the literature is quoted), and the quantitative relations of the various products (Harden, Chem. Soc. Trans. 1901, 612; J. Hygiene, 1905, 5, 488). The following are the results obtained by Harden for the action of an organism of the *B. coli* group on glucose, fructose, and mannitol, and for *B. typhosus* on glucose. The coli-like organism employed in these experiments fermented cane sugar and not dulcitol, and would therefore now be regarded as *B. coscoroba*. The products are expressed in percentages of the sugar fermented and also in terms of the number of carbon atoms of the sugar molecule represented by the product. The cultivations were all carried out in an atmosphere of nitrogen, to avoid atmospheric oxidation, and in presence of chalk to neutralise the acid produced, and thus to obtain a more complete utilisation of the sugar present. The carbon dioxide evolved by the action of the acid on the chalk has, in every case, been subtracted. The products in all cases were qualitatively the same.

The characteristics of the fermentation of glucose by this coli-like organism are that the lactic acid forms less than half of the total products, that alcohol and acetic acid are produced in almost molecular proportions, and that the ratio of hydrogen to carbon dioxide by volume is almost 1. *B. typhi* produces a similar change, with the exception that no gas is formed but an equivalent amount of formic acid is produced. Since *B. coli* and the allied *B. coscoroba* have the power of decomposing formates with the production of equal volumes of carbon dioxide and hydrogen, this would indicate that most probably formate is produced in all cases, but decomposed by *B. coli* and its allies, and left untouched by *B. typhi*. This is confirmed by the fact that small quanti-

Product	*B. coscoroba*						*B. typhi*	
	Glucose		Fructose		Mannitol		Glucose	
	Per cent.	C atoms	Per cent.	C atoms	Per cent.	C atoms	Per cent.	C atoms
Lactic acid	31·90	1·91	48·20	2·89	18·600	1·13	49·5	2·96
Succinic acid	5·20	0·32	6·10	0·37	8·900	0·55	trace	trace
Acetic acid	18·84	1·13	16·10	0·97	9·500	0·58	12·7	0·76
Alcohol	12·85	1·01	11·50	0·90	28·100	2·22	9·1	0·70
Formic acid	—	—	trace	trace	3·000	—	17·7	0·69
Carbon dioxide	18·09	0·74	13·07	0·53	28·440	1·28	—	—
Hydrogen	0·01	—	—	—	0·015	—	—	—

ties of formic acid are often produced by the gas-forming organisms, and are increased when the cultivation is carried out under pressure.

The production of acetic acid and alcohol from glucose in approximately molecular proportions is characteristic of a large number of the organisms of this group, *B. coli communis*, *B. acidi lactici*, *B. coscoroba*, *B. Neapolitanus*, and *B. typhi*, all presenting this peculiarity (Harden).

The case of mannitol is interesting, as the effect of the change in constitution from glucose to mannitol is that the production of alcohol and carbon dioxide is almost doubled, whilst that of acetic and lactic acids is greatly diminished. Other types of intestinal organisms, for example, the various types of dysentery bacilli, which are much more restricted in their power of fermentation, produce somewhat similar effects on glucose, but in some cases much more lactic acid is produced, whilst alcohol and acetic acid are formed in a different ratio. Such types of fermentation appear to be intermediate between the true lactic fermentation and that just described.

Production of butylene glycol. Several species of intestinal bacteria differ in a very marked manner from the foregoing types, inasmuch as they produce large quantities of $\beta\gamma$-butylene glycol $CH_3{\cdot}CH(OH){\cdot}CH(OH){\cdot}CH_3$, along with small quantities of the corresponding ketoalcohol, acetylmethylcarbinol

$$CH_3{\cdot}CO{\cdot}CH(OH){\cdot}CH_3.$$

This latter substance, in presence of oxygen and alkali, gives a characteristic colour reaction with proteins, known as Voges and Proskauer's reaction. The following quantitative results have been obtained with *B. lactis aërogenes* (Escherich) and similar ones are given by *B. cloacæ* (Jordan), (Harden and Walpole, Proc. Roy. Soc. 1906, B, 77, 421; Walpole, *ibid.* 1911, B. 83, 272; Thompson, *ibid.* 1912, B, 84, 500; Harden and Norris, *ibid.* 1912, B, 84, 492):—

	Glucose		Mannitol	
	P.c.	C atms	P.c.	C atms.
Alcohol	18·2	1·43	32·5	2·57
Acetic acid	8·6	0·52	2·1	0·12
Lactic acid	9·1	0·55	8·6	0·52
Succinic acid	4·5	0·27	2·8	0·17
Formic acid	1·7	1·21	1·6	1·53
Carbon dioxide	35·2		35·5	
Hydrogen	0·01	—	—	—
Butyleneglycol (by dif.)	(22·7)	1·72	(16·9)	1·19
Vol. ratio of H_2/CO_2	0·52	—	0·79	—

This type of fermentation, therefore, is characterised alike by the large production of alcohol and the formation of butylene glycol. As in the case of the coli-like organisms, the alcohol produced from mannitol is approximately twice as much as from glucose. It seems not improbable that this relation is connected with the occurrence of the terminal group $\cdot CH(OH){\cdot}CH_2{\cdot}OH$ twice in mannitol and only once in glucose. The ratio of H_2/CO_2 is also much lower than is observed with the coli-like organisms.

Many bacilli not of intestinal origin also give rise to similar products. Thus, Tate (Chem. Soc. Trans. 1893, 1263) found that an organism derived from ripe pears fermented glucose and mannitol to alcohol, acetic, formic, succinic, and *l*-lactic acids, and made the interesting observation that rhamnose, a methylpentose

$CH_3{\cdot}CH(OH){\cdot}CH(OH){\cdot}CH(OH){\cdot}CH(OH){\cdot}CHO,$

was decomposed by the same organism, but yielded no alcohol or formic acid, the products consisting of acetic, succinic, and *dl*-lactic acids. In no case did the sum of the products obtained by Tate approach the weight of the material fermented, the discrepancy being from 20–60 p.c. Again, the pneumobacillus of Friedländer (*B. pneumoniæ*) was found by Grimbert (J. Pharm. Chem. 1895, [6] 2, 529) to yield 36–58 p.c. of *l*-lactic acid from glucose and mannitol, along with alcohol, and acetic acid; whilst Frankland, Frew, and Stanley (Chem. Soc. Trans. 1891, 253) obtained no lactic acid, but only alcohol, acetic, succinic, and formic acids and a large volume of carbon dioxide and hydrogen, the products from mannitol being in the ratio

$$9C_2H_6O : 4C_2H_4O_2 : 10CO_2 : 8H_2,$$

whilst relatively less alcohol was formed from glucose. The discrepancy between these results probably points to imperfect identification of the organism on the part of one or other of these observers or else to a wide difference in chemical action between different varieties of the same organism.

(c) **The butyric fermentation.** Normal butyric acid and normal butyl alcohol are formed from carbohydrates, higher alcohols, glycerol, lactic acid, and other compounds by the action of many bacteria, and, in addition to this, organisms are also known which produce butyric acid from proteins. The bacteria which produce butyric acid from carbohydrates are characterised by an extreme tendency to variety and multiplicity of form, and this has given rise to the greatest confusion in the literature of the subject, and to considerable difficulty in the identification of species.

The butyric fermentation, well known as a means of preparing butyric acid by the inoculation of a glucose solution with decaying cheese, was first ascribed to a specific organism by Pasteur (1861). He named this organism the *Vibrion butyrique*, and made the highly important observation that its motility was destroyed by the presence of oxygen, a phenomenon which led to the recognition of the existence of anaërobic organisms and to Pasteur's celebrated theory, 'La fermentation est la vie sans air.' The subsequent researches of Prazmowski, Grüber, Botkin, Beyerinck, Flügge, and many others, added to the *Vibrion butyrique* of Pasteur as producers of butyric acid a large number of species of varying forms and properties. A considerable degree of simplification has, however, been introduced into this somewhat complex group of organisms by the exhaustive investigations of Schattenfroh and Grassberger (Arch. Hyg. 1900, 37, 54).

Limiting their consideration to anaërobic bacteria producing butyric acid from non-nitrogenous sources, they recognise only two main types of organism. 1. The *non-motile butyric acid bacillus* occurs regularly in cow-dung, and is therefore to be found in milk and is also present in the soil. The organism presents two types of growth, long, thick rods

or shorter and more slender forms, is anaërobic, liquefies gelatin, and on starch paste agar forms spores which withstand boiling for 1·5 hours. It is, however, extremely variable and readily forms the so-called clostridia or shuttle-shaped forms. The cells when grown on starch at the optimum temperature of 37° contain granulose or iogen granules, which stain blue with iodine, and probably consist of a reserve carbohydrate.

Schattenfroh and Grassberger regard this organism, which includes in its various forms those previously known as *Granulobacter lactobutyricum* (Beyerinck), *B. enteritidis sporogenes* (Klein), and *B. aërogenes capsulatus* (Welch), as a denaturised form of the bacillus of symptomatic anthrax, an organism pathogenic to cattle, which, in its native state, is motile. It ferments the sugars and starch, but not mannitol or cellulose, and attacks glycerol, and in some of its intermediate forms also ferments lactic acid, the products being usually butyric acid, *d*-lactic acid, carbon dioxide, and hydrogen.

2. *The motile butyric acid bacillus* is found in soil, water, and cheese, but less frequently in milk, and also occurs in a great variety of forms, from rods to clostridia, and yields at least three types of growth on gelatin, which it does not liquefy. Like the non-motile bacillus, it is anaërobic, forms spores, produces granulose, and grows well at 37°. It comprises the organisms previously known as *B. amylobacter* (Grubor), *Granulobacter saccharobutyricum* (Beyerinck), and *B. saccharobutyricus* (Klecki), and probably the *Clostridium butyricum* of Prazmowski, and the *Vibrion butyrique* of Pasteur. Its chemical action is much the same as that of the non-motile bacillus. In addition to these two types, the *B. œdematis maligni* (Koch), which is pathogenic, also produces butyric acid from carbohydrates, and the *B. putrificus* (Bienstock), from proteins (*see Putrefaction*).

A number of aërobic organisms capable of forming butyric acid are also known, chief among these being the *B. butyricus* (Hueppe), but it appears doubtful whether this organism produces the butyric acid from carbohydrates or from the proteins also present, no quantitative experiments having been made.

The *B. butylicus* of Fitz (Ber. 1878, 11, 49), obtained from hay infusion, decomposes glucose, glycerol, mannitol, and saccharose, but not lactose, or lactic, malic, glyceric, or tartaric acids. Fitz, working with a culture of somewhat doubtful purity, obtained the following results with glycerol, mannitol, and invert sugar:—

	Glycerol p.c.	Mannitol p.c.	Invert sugar p.c.
n-Butyl alcohol	8·1	10·2	0·5
n-Butyric acid	17·4	35·4	42·5
Lactic acid	1·7	0·4	0·3
Succinic acid	—	0·01	trace
Trimethylene glycol	3·4	—	—

The fermentation of glycerol by this organism has been recommended by Fitz, and subsequently by Freund, as a convenient method for the preparation of *n*-butyl alcohol and of trimethylene-glycol.

Buchner and Meisenheimer (Ber. 1908, 41, 1410), also working with the *B. butylicus* of Fitz, obtained analogous results, as did also Perdrix (Ann. Inst. Pasteur, 1895, 5, 286) with the *B. amylozyma* (Perdrix).

	Glycerol	Glucose
n-Butyl alcohol	19·6	0·7
Ethyl alcohol	10·4	2·8
Carbon dioxide	42·1	48·1
Hydrogen	1·9	1·6
Formic acid	4·0	3·4
n-Butyric acid	0·7	26·0
Acetic acid	1·0	7·5
Lactic acid	3·4	10·0

The production of butyric acid and butyl alcohol from glycerol and lactic acid by means of the butyric bacillus is of great theoretical importance, since it involves a synthesis from the primary products of the rupture of the carbon chain. It has been suggested by many observers that one of these is acetaldehyde, from which the butyric acid and butyl alcohol could readily be formed by an aldol condensation, followed by reduction or a combined oxidation and reduction:

$$2CH_3\cdot CHO = CH_3\cdot CH(OH)\cdot CH_2\cdot CHO.$$

$$CH_3\cdot CH(OH)\cdot CH_2\cdot CHO + 4H = CH_3\cdot CH_2\cdot CH_2\cdot CH_2(OH) + H_2O$$

That lactic acid is not necessarily an intermediate product in the butyric fermentation, as suggested by Buchner and Meisenheimer, is shown by the fact that certain organisms will not ferment lactic acid in this way, although they produce butyric acid from sugars. The detection of anaërobic butyric acid bacteria in milk (Klein's *B. enteritidis sporogenes*) forms part of the routine examination of milk for fæcal contamination, and is carried out by heating the milk to 80° for 10 minutes to destroy all vegetative forms and leave only the resistant spores, and incubating measured quantities of the liquid anaërobically. A characteristic separation of the caseinogen in flocculi, accompanied by a smell of butyric acid and the development of Gram-positive rods pathogenic to guinea-pigs, indicates the presence of the bacillus.

(*d*) **The fermentation of cellulose and bacterial production of methane.** The bacterial fermentation of cellulose takes place on a vast scale in the soil, especially in marshy places, and appears to be one of the chief processes by which the cellulose of plant remains is resolved into simpler products. It is to this decomposition that is due the evolution of an inflammable hydrocarbon from marshes, which was first recognised by Volta in 1776. A similar decomposition occurs in the stomachs of graminivorous animals (Tappeiner) and in heaps of manure, wool refuse, &c. The fact that cellulose was capable of undergoing fermentation was first observed by Mitscherlich in 1850, who ascribed the gradual disappearance of the cell walls of potatos left in water for several days to the action of bacteria. The power of destroying cellulose was subsequently (erroneously) attributed by van Tieghem (Compt. rend. 1879, 88, 205; 89, 25, 1102) to the *B. amylobacter* (Gruber), on the ground of the destructive action of this bacillus on many vegetable tissues. A considerable amount of information as to the chemical nature of the process of cellulose fermentation was afforded by the researches of Popoff (Arch. Phys. 1875, 10, 113), Tappeiner (Ber. 1881, 2375; 1882, 999; 1883, 1734; 1884, 142, 262, 587), and Hoppe-Seyler (Zeitsch. physiol.

Chem. 1886, 10, 201, 401; Ber. 1883, 16, 122). Popoff and Hoppe-Seyler worked with sewer mud, and found that it contained organisms capable of decomposing Swedish filter paper, and producing from it carbon dioxide, methane, and sometimes hydrogen. Hoppe-Seyler, indeed, was able to bring about the conversion of 25·8 grams of pure filter paper into marsh gas and carbon dioxide in 4 years at room temperature, no other products being formed. Tappeiner paid attention chiefly to the extremely interesting problem of the decomposition of cellulose in the animal intestine, which had previously been ascribed to the action of a soluble enzyme (Hofmeister). He showed that a large part, if not the whole, of this decomposition, which in ruminants may amount to as much as 75 p.c. of the cellulose ingested, is bacterial and is accompanied by the evolution of large volumes of carbon dioxide, marsh gas, and sometimes hydrogen. He was moreover able to show that two types of cellulose fermentation existed, one of which was characterised by the production of methane, the other by that of hydrogen, methane being formed when the nutrient medium contained beef extract, hydrogen when only salts of known composition were used. In both cases carbon dioxide was evolved, and aldehyde and large quantities of acetic and butyric acids were produced. No advance had, up to this time, been made in the determination of the specific bacteria to which the destruction of cellulose was due, this function being generally ascribed to *B. amylobacter*, although van Senus (Koch's Jahrb. 1890, 1, 136) considered that the presence of a second organism was necessary. Much light has been thrown on the whole subject by the long-continued researches of Omelianski (Centr. Bakt. Par. Abt. ii. 1902, 8, 193; 1904, 11, 369; 12, 33; 1906, 15, 673; article in Lafar, Technische Mykologie, 1904, iii. 245). Omelianski has found that the fermentation of cellulose is produced by anaërobic sporing bacteria, and agrees with Tappeiner in recognising the methane and hydrogen types of fermentation. These are brought about by different organisms, which can be separated if advantage be taken of the fact that when a mixed culture of the spores of both varieties, such as occurs naturally in sewer mud or manure, is inoculated into the nutrient solution described below, and cultivated anaërobically, the bacteria of the methane fermentation are the first to grow. Accordingly, when such a mixed culture is allowed to develop and is then heated to 75° for 15 minutes, the vegetative forms of the methane bacteria are killed, and a succession of inoculations and heatings suffices to remove the whole of these, and leaves a culture which produces a pure hydrogen fermentation. On the other hand, direct inoculation without heating leads to the elimination of the undeveloped spores of the hydrogen organism and the production of a pure methane fermentation. It has not so far been found possible to obtain cultures of either form on solid media, and Omelianski relies on the strongly selective character of his medium and the microscopic appearance of his cultures as the only guarantees of their purity. The medium found suitable consists of potassium phosphate, 1 gram; magnesium sulphate, 0·5 gram; ammonium sulphate or phosphate, 1 gram; sodium chloride, trace; distilled water, 1 litre. To 300 c.c. of this, 3–4 grams of Swedish filter paper and 5–6 grams of chalk are added, and the whole inoculated. The fermentation only begins after at least a week's incubation, and proceeds slowly for many months. Spots slowly appear on the paper, and these gradually become perforations, and the paper breaks up into fragments and finally disappears. The decomposing fragments are found to be densely covered with bacteria, which are very slender, isolated rods, those of the methane fermentation being somewhat the thinner of the two species. They gradually produce at one end a round spore, three times the diameter of the rod (drumstick form). The bacilli can be stained by the ordinary aniline dyes, and do not give a blue colouration with iodine.

In the absence of any isolation of the bacteria on solid media or cultivation from a single spore, it must still be regarded as doubtful whether either of these organisms has yet been obtained in pure culture.

The products of decomposition of cellulose were examined quantitatively by Omelianski, and found to be as follows:—

	Hydrogen fermentation	Methane fermentation
	p.c.	p.c.
Carbon dioxide	29·1	43·2
Hydrogen	0·4	—
Methane	—	6·8
Acetic acid	35·9	43·6
Butyric acid	31·0	7·1
	96·4	100·7

Much remains yet to be learnt of the nature and conditions of the process of cellulose fermentation; in particular it has not been ascertained whether the cellulose is rendered soluble before being fermented, and if so by what means. Cellulose is, however, also attacked and disintegrated by various aërobic organisms and by certain moulds, but little is known as to their mode of action. The materials containing the cellulose-fermenting bacteria also contain organisms which are capable of producing methane from a great variety of substances, among which are acetates (Hoppe-Seyler), butyrates (Mazé), gum arabic (Omelianski), and, according to Tappeiner, various albumins and protein derivatives. Omelianski also obtained from decaying wood organisms which produced methane fermentation with egg albumin, glue, gelatin, wool, and peptone. Fermentations of this kind undoubtedly play a large part in the destruction of animal and vegetable remains, and are of great technical importance in the decomposition of sewage in the septic tank and in the fermentation of manure. An interesting consequence of their constant occurrence in nature is the presence of methane in the air, as much as 11·3 c.c. per 100 litres having been found by Gautier in the air of wooded rural districts, where the decomposition of vegetable matter in the soil is probably very considerable.

Other types of fermentation by decomposition. Fermentation of the hydroxy-acids and glycerol. Among the numerous other types of fermentation involving the rupture of the carbon chain of non-nitrogenous compounds, only a few can be mentioned here.

i. The *B. ethaceticus* (F.) was isolated in 1890 from sheep dung by Frankland, who carefully examined its action on a number of different substances. This organism does not appear to have been identical with any of the more recently described intestinal bacteria. It fermented glucose, mannitol, arabinose, and glycerol, forming mainly acetic acid, alcohol, formic acid, and a mixture of equal volumes of carbon dioxide and hydrogen. No lactic acid was produced, but from glucose and arabinose a fixed acid of unknown composition was probably formed (Frankland and Fox, Proc. Roy. Soc. 1890, 46, 345; Frankland and Frew, Chem. Soc. Trans. 1891, 81; Frankland and Lumsden, *ibid.* 1892, 432; Frankland and MacGregor, *ibid.* 1892, 737). This organism had the interesting property of fermenting a solution of calcium *dl*-glycerate asymmetrically, only decomposing the *l*-acid and leaving unattacked the pure *d*-acid, which was first isolated in this way. The decomposition is represented by the equation:

$$5C_3H_6O_4=C_2H_6O4+C_2H_4O_2+5CO_2+3H_2+H_2O.$$

This organism, after repeated cultivation in calcium glycerate, however, acquired the power of slowly fermenting the *d*-acid.

ii. *Glycerol* undergoes fermentation by many organisms, and in some cases yields butyric acid, as has already been described.

A more usual change is its decomposition mainly into alcohol and formic acid or carbon dioxide and hydrogen:

$$C_3H_8O_3=C_2H_6O+CO_2+H_2.$$

This was observed by Fitz with an organism known as *B. ethylicus* or *Fitzianus*, and this is also the type of decomposition produced by *B. coli communis* (Harden).

iii. *The hydroxy-acids*, such as lactic acid, malic acid, and citric acid, are readily decomposed by many organisms. Thus lactic acid, in addition to undergoing butyric fermentation, is converted by a mixed fermentation (Strecker, 1854, Fitz) into acetic acid, propionic acid, and carbon dioxide. Malic acid yields with *B. lactis aërogenes*, carbon dioxide, acetic acid, and a large amount of succinic acid (Emmerling), similar products being formed by *B. cloacæ* (Thompson), whilst citric acid is converted by these two organisms into carbon dioxide and acetic acid.

iv. *The mannitol fermentation* is effected by an organism which occurs as an infection in wines (Gayon and Dubourg, Ann. Inst. Past. 1894, 8, 108; 1901, 15, 527). It decomposes sugars into alcohol, carbon dioxide, acetic, lactic, and succinic acids, and glycerol, but with fructose yields a considerable proportion of mannitol.

3. Fermentations by Oxidation.

All aërobic organisms have the power, like the higher plants and animals, of oxidising appropriate food materials, with production of carbon dioxide and water. It is, however, frequently possible, in the case of bacteria, to isolate partially oxidised products and thus ascertain some of the stages of the process, whereas this can only rarely be accomplished with higher organisms. The production of acetic acid from alcohol by bacterial action is one of the most important cases of this kind; the conversion of ammonia into nitrous acid, and this into nitric acid, being a second.

(*a*) **The acetic fermentation of alcohol and the oxidising properties of the bacteria which produce it.** The spontaneous souring of wine, beer, and other alcoholic liquors when exposed to air has long been known and employed for the manufacture of vinegar. Pasteur, in 1864 (Mém. sur la fermentation acetique; Ann. École Norm. sup. 235, 225; J. Chem. Soc. Abstr. 1881, 128; Études sur le vinaigre, 1868), conclusively proved that the change of alcohol into acetic acid in this process was due to the 'flowers of vinegar,' an organism which, from the circumstance that it formed a film on the surface of the liquid, he termed *Mycoderma aceti*. Pasteur carefully examined this organism, cultivated it in synthetic media, and proved that it acted as a carrier of oxygen from the air to the alcohol, and that it was capable, when no more alcohol was available, of oxidising the acetic acid to carbon dioxide and water. Traces of aldehyde were observed to be produced when the vitality of the organism was impaired. Since Pasteur's time a large number of organisms have been found which have a similar action on alcohol, and which include those found in vinegar breweries. These are not very clearly characterised, and only one or two of the most important can be here mentioned (*see* Henneberg, various papers in Centr. Bakt. Par. Abt. ii. 1897–98, 1905–6; and Gärungsbacteriologisches Praktikum, Berlin, 1909, 510–558). *B. aceti* (Hansen) has been studied morphologically by Cohn (Biol. d. Pflanzen, 2, 173), and biochemically by A. J. Brown (Chem. Soc. Trans. 1886, 174; 1887, 638) and Hansen. It grows on the surface of culture media, forming an easily broken film, consisting of chains of cells about 2 inches in length, and slightly contracted in the middle, so that they resemble a figure of 8. It does not form spores, and readily produces involution forms, cells of 10–15 μ in length and irregularly swollen being common. As regards the production of acetic acid from alcohol, Brown fully confirmed Pasteur's observations with *Mycoderma aceti*. The highest concentration of acetic acid that can be obtained by the use of this organism is 6·6 p.c. (Henneberg).

Brown also found that this organism converts *n*-propyl alcohol into propionic acid, and glycol into glycollic acid, but does not act on methyl alcohol or erythritol, whilst it oxidises glycerol completely. The observation that this bacillus converts glucose into gluconic acid (Boutroux, Compt. rend, 1878, 86, 605; 1880, 91, 236) was confirmed. Mannitol undergoes an extremely interesting reaction, being converted into fructose. All these reactions occur when the organism is grown on solutions of the various substances in yeast water, chalk being added to neutralise the acids formed.

As already mentioned, Buchner and Gaunt (Annalen, 1906, 349, 140) have shown that the oxidation of alcohol by this organism is due to the action of an enzyme, and can be effected by the cells after they have been killed and dehydrated by acetone.

B. xylinus (Brown) is the organism which occurs in the vinegar plant, or mother of vinegar, in which it is associated with a yeast. The mixed growth is thus capable of converting cane sugar solution into vinegar, the sugar, which is

itself not attacked by the bacillus, being hydrolysed and fermented by the yeast, with production of alcohol, which is then oxidised by the bacillus. The *B. xylinus* in pure culture grows on the surface of alcoholic liquids, forming thick, tough gelatinous membranes, which sometimes on wine attain a thickness of as much as a foot. This is due to the formation of a transparent film in which the short, rod-like bacilli are embedded. This film contains a large proportion (35–62 p.c. of its dry weight) of cellulose (Brown), and is formed from glucose, fructose, and mannitol, but not from cane sugar or starch. The cellulose formed from fructose yielded glucose when hydrolysed with acids. The chemical actions of this organism were found by Brown to agree in general with those of *B. aceti*. They have been more completely investigated by Bertrand (Ann. Chim. Phys. 1904, [8] 3, 181), who terms the organism the sorbose bacterium. He finds that this organism converts many polyvalent alcohols into the corresponding *a*-ketose, thus changing sorbitol into sorbose, mannitol into fructose, *i*-erythritol into erythulose $CH_2(OH)\cdot CO\cdot CH(OH)\cdot CH_2OH$, *l*-arabitol $C_5H_{12}O_5$ into arabinulose $C_5H_{10}O_5$, perseitol and volemitol $C_7H_{16}O_7$, into perseulose and volemulose $C_7H_{14}O_7$. Of great interest is its action on glycerol, which it converts into dihydroxyacetone $CH_2(OH)\cdot CO\cdot CH_2\cdot OH$, entirely free from the isomeric glyceraldehyde which is invariably formed by the action of ordinary oxidising agents.

This method is by far the most convenient for the preparation of dihydroxyacetone, the organism being simply grown for about 3 weeks on a 10 p.c. solution of glycerol in yeast water, and the liquid then evaporated, precipitated by alcohol, filtered and finally evaporated *in vacuó*.

On the other hand, glycol, *l*-xylitol, and *d*-dulcitol are not attacked. The action of the bacillus is confined to the oxidation of a secondary carbinol group, which is not stereochemically in the neighbourhood of a hydrogen atom (Bertrand). The aldoses are oxidised to the corresponding acid, glucose, xylose, arabinose, and galactose all behaving normally in this respect. When the acid thus produced contains a CH(OH) group capable of being attacked, according to the rule just stated, this may also be oxidised. Thus gluconic acid yields the corresponding ketonic acid, oxygluconic acid $CH_2(OH)\cdot CO\cdot CH(OH)\cdot CH(OH)\cdot CH(OH)\cdot COOH$, which had previously been obtained by Boutroux by the aid of the *M. oblongus* (Bout.) (Compt. rend. 1886, 102, 924).

(*b*) **Nitrification.** The conversion of the nitrogen of organic matter into nitrates in the soil was familiar to chemists at a very early date, and was employed as a means of manufacturing saltpetre. From the time of Mayow onwards, it was regarded as a purely chemical action brought about by the agency of the porous soil, or, according to Liebig's characteristic view, by a ferment, *i.e.* some substance which was itself undergoing oxidation in the soil. The idea that this process was in reality of biological origin was suggested by Pasteur (1862), but first more fully developed by Schloesing and Müntz (Compt. rend. 1877, 84, 301; 1878, 86, 392; 1879, 89, 891, 1074), who found that nitrification ceased when the soil was sterilised by heat or antiseptics. The researches of Warington (Chem. Soc. Trans. 1878, 44; 1879, 429; 1884, 637; 1888, 727), carried out at Rothamsted, contributed, along with much information as to the conditions of nitrification, the fundamentally important facts that oxidation often only proceeded as far as the production of nitrite, and that the nitrogen was converted into ammonia before being nitrified. These conceptions were then further developed by Munro (Chem. Soc. Trans. 1886, 632), who came to the conclusion that the normal course of nitrification consisted in the production of ammonia followed by that of nitrites and nitrates. Up to this time (1888), all attempts to isolate the organisms by the aid of which the change was effected had failed, and it was not until this had been effected by Winogradsky (Ann. Inst. Past. 1890, 4, 213; article in Lafar, Technische Mykologie, 1904, iii. 132–181), and almost simultaneously by Warington (*see* Chem. Soc. Trans. 1898, 484), that the true conditions of the process were discovered. The bacillococcus possessed of nitrifying power which was described by P. and G. Frankland (Proc. Roy. Soc. 1890, 47) was subsequently found not to be a pure culture. Winogradsky, convinced that the presence of organic matter was detrimental to the development of the organism, inoculated with earth a solution containing only 1 per mille of ammonium sulphate and of potassium phosphate, together with some solid basic magnesium carbonate, and by repeated sub-cultivations succeeded in obtaining strong nitrification in a liquid almost free from organisms capable of growing on the ordinary solid media. The principle involved is that of selective culture, only those organisms surviving which can avail themselves of the very limited supply of nourishment provided. The deposit of magnesium carbonate in such solutions was observed to be covered with gelatinous masses of the nitrifying organism, and when this was spread on gelatin, it was found that many particles produced no growth whatever, and were therefore free from all ordinary soil organisms. Some of these, when removed and placed in the culture fluid, produced active nitrification, and a growth in which no foreign organisms could be detected. It was subsequently found by Winogradsky that this organism was only capable of converting ammonia into nitrite, and that the final stage of the oxidation to nitrate was effected by a second organism, which was isolated (1891) in a similar manner, by repeated sub-culture in a selective culture medium containing sodium nitrite instead of an ammonium salt. This discovery led to the explanation of the apparently capricious action of the nitrifying organisms, which sometimes yielded nitrite and at others nitrate. It was found, in confirmation of the opinion expressed by Warington, that the development of the nitrate-producing organism was inhibited by comparatively small proportions of ammonium salts. This effect is, in fact, very remarkable, and is comparable to that of the most powerful antiseptics. In a particular case as little as 0·005 gram per litre of ammonia (as sulphate) caused a perceptible diminution in the rate of nitrification of a nitrite solution, and 0·154 gram completely inhibited it. On the other hand, nitrites may be present up to at least 10 grams per litre, and nitrates to 20 gram

per litre. When, however, ammonia is added to a liquid containing a well-developed culture of the nitrate-producing organism, it causes very little change in the rate of action, even in quantities of 1·8 grams per litre, so that its harmful effect is mainly one of inhibition, exerted on the development of the organism, and not on the oxidising action of the developed organism (Winogradsky).

In agreement with these facts, it is found that when an inoculation of earth is made into solutions of ammonium salts, nitrosification (the production of nitrite) proceeds until nearly all the ammonia has been converted, and only then does the production of nitrate begin. The repeated addition of fresh ammonia before this second stage sets in will limit the action entirely to the production of nitrite. If, however, nitrate production is once well established, further additions of ammonia are completely converted into nitrate. Similar conditions prevail in the nitrification of sewage, which is apparently effected by the same organisms as are found in the soil (Chick, Proc. Roy. Soc. 1906, B, 77, 241).

Another remarkable feature of these organisms is their mode of carbon assimilation. Organic carbon not only cannot be assimilated by them, but actively inhibits their development, compounds such as glucose and peptone totally inhibiting nitrosification in concentrations of 0·2 p.c. and nitrification in concentrations of 0·25 p.c. (glucose), and 1·25 p.c. (peptone), and behaving, therefore, in this respect like powerful antiseptics. It was this property which rendered the isolation and artificial culture of these organisms so difficult. The sole source of carbon for both classes of organism appears to be carbon dioxide, derived from carbonates by the nitrosifying organism, and from bicarbonates by the nitrifying organism. The energy necessary for the reduction of carbon dioxide to assimilable compounds is apparently provided by the oxidation of the ammonia or nitrite, and a fixed ratio exists between the amounts of carbon assimilated and ammonia or nitrite oxidised. Thus the nitrosifying organism oxidises 35·4 parts of nitrogen as ammonia for 1 part of carbon assimilated (Winogradsky).

The study of the morphological characteristics of the organisms of this highly important group has been greatly aided by the discovery of solid media on which cultivations can be made. Winogradsky first introduced a jelly of silica saturated with the culture fluid, and Omelianski has successfully used plates made of gypsum and 1 p.c. of magnesium carbonate, and even discs or strips of filter paper. More convenient are the agar plates introduced by Beyerinck (Cent. Bakt. Par. ii. 1896, 19, 258). The agar-water jelly is allowed to stand for about a fortnight under water. Fermentation occurs, accompanied by the decomposition of all the compounds which inhibit the growth of the nitrifying organisms. The agar is then washed, mixed with the culture medium and a little chalk, and finally sterilised.

The exact relations of the various organisms which have been isolated are still unknown. The general result is that several nitrosifying organisms have been obtained from different regions, whereas hitherto only one nitrifying organism has been found. The nitrosifying organism is termed *B. nitrosomonas* (Winog.), L. and N. The forms of the West European variety are oval bacilli ($1 \times 1{\cdot}2$–$1{\cdot}8\mu$), which produce zooglœa in fluid media, and brown colonies on solid media; these break up after some time into motile forms. The organism from Buitenzorg in Java, on the other hand, is a minute micrococcus $0{\cdot}5$–$0{\cdot}6\mu$ in diameter, and that from Quito a large coccus $1{\cdot}5$–$1{\cdot}7\mu$ in diameter, which does not form zooglœa. The organism from Japan closely resembles the European variety. Hitherto only one variety of this organism has been obtained in any one district.

B. nitrobacter (Winog.), L. and N., which converts nitrites into nitrates, is a bacillus $1 \times 0{\cdot}3$–$0{\cdot}4\mu$, possesses a gelatinous capsule, and never forms motile cells. It grows very slowly on agar, forming almost colourless, drop-like colonies.

(*c*) **Other oxidising effects produced by bacteria. Oxidation of sulphuretted hydrogen, ferrous oxide, hydrogen, and methane.** Very special interest attaches to the action of bacteria in bringing about the oxidation of sulphuretted hydrogen. This process is comparable with the nitrification of ammonia, inasmuch as it has the effect of converting sulphuretted hydrogen, a direct product of the putrefaction of proteins, into sulphates, from which plants are able to supply themselves with the sulphur essential for their growth.

Early observers noted the occurrence of characteristic micro-organisms in sulphur wells, and the presence of granules of sulphur within their cells (1870–1875), but it is to the researches of Winogradsky that we owe, in the main, our present knowledge of the sulphur bacteria. The oxidation of sulphuretted hydrogen is effected in two stages. The first product is free sulphur, which is deposited in the cell in the form of soft spherical granules of amorphous sulphur. In the presence of abundance of sulphuretted hydrogen, the cell becomes crowded with these particles. The second stage consists in the oxidation of this sulphur to form sulphuric acid, which neutralises the carbonates present in the soil to form sulphates. It seems probable that these organisms derive the whole of their carbon from carbon dioxide, the energy necessary for its decomposition being derived from the oxidation of the sulphuretted hydrogen. Many genera of sulphur bacteria are known, the most important being *Beggiatoa* and *Thiothrix*, which form long threads, and are regarded by some authors as intermediate between the bacteria and algæ. In addition to these, a large number of others have been described, many of which are characterised by the production of a red colouring matter known as bacteriopurpurin (Ray Lankester).

Another group of bacteria is known, the species of which bring about the oxidation of ferrous hydrogen carbonate to ferric hydroxide in chalybeate waters. These organisms, which, like the sulphur bacteria, form long threads, are also closely allied to the algæ, and belong to the genera *Crenothrix*, *Cladothrix*, *Streptothrix*, &c. They are also able to effect the oxidation of manganese salts, and the resulting oxides are apparently deposited in the gelatinous membrane of the cell (Molisch, quoted by Rullmann, Lafar, iii.).

Other groups of bacteria are able to play the part of platinum black in bringing about the oxidation of hydrogen (Lebedew, Biochem. Zeitsch. 1907, 7, 1; Lebedew and Nabokich Centr. Bakt. Par. ii. 1906, 17, 350; Niklewski, Centr. Bakt. Par. ii. 1907, 21, 380), whilst others can effect the oxidation of marsh gas, and an organism has been described by Beyerinck (*ibid.* ii. 1909, 25, 30), which can bring about reaction between nitrous oxide and hydrogen, and obtain its carbon from carbon dioxide by the aid of the energy thus liberated.

4. Fermentations by Reduction and Deoxidation.

(*a*) **Reduction.** The decomposition of a molecule of a carbon compound into two or more smaller molecules, some of which are relatively more oxidised and others relatively more reduced, is, as we have seen, a common feature of many fermentations by decomposition. A typical example is afforded by the alcoholic fermentation of sugar, which results in the formation of carbon dioxide on the one hand, and alcohol on the other. The decomposition sometimes results in the production of free hydrogen, and when this occurs in the presence of reducible substances, reduction often takes place. Of this secondary character are the reduction by *B. coli communis* of nitrates to nitrites in presence of sodium formate (Pakes and Jollyman, Chem. Soc. Trans. 1901, 459), and of aspartic acid in presence of glucose to ammonium succinate (Harden, *ibid.* 1901, 612), the reduction being effected by the hydrogen produced from the formate and glucose respectively. Many similar cases are known, especially among mixed fermentations (see Söhngen, Rec. trav. chim. 1910, 29, 238). In other cases the reducing action of bacteria is exercised directly upon the reducible compound, and results either in the direct removal of oxygen or the addition of hydrogen. In the former case the oxygen probably goes to produce physiological oxidation in the bacterial cell. Thus many aërobic organisms can grow in the absence of free oxygen, provided that nitrates are added to the medium, and these are thereby converted into nitrites (Pakes and Jollyman, Chem. Soc. Trans. 1901, 322; Ritter, Centr. Bakt. Par. ii. 1907–8, 20, 21).

The bacterial reduction of sulphates, thiosulphates, and sulphites to sulphuretted hydrogen is probably due to a similar action (Beyerinck, *ibid.* 1895, 1, 1).

The direct addition of hydrogen by bacteria to certain colouring matters is a well-recognised phenomenon. Thus many organisms readily reduce methylene blue to the leuco-compound, not only when grown in its presence, but also when the organisms are suspended in a solution of the colouring matter. The same effect is produced by dry sterile preparations obtained by treating the bacteria with acetone, and is ascribed to the action of a specific reducing enzyme or reductase, which becomes inactive at about 60° (Cathcart and Hahn, Arch. Hyg. 44, 296). The exact chemistry of the process has not been worked out, but the most probable source of the hydrogen is water, the oxygen of which is thus rendered available for oxidations in the cell. Reducing enzymes also occur in many animal tissues and plants, but little is known as to their mode of action (*see* Bach. Biochem. Zeitsch. 1911, 31, 443).

(*b*) **Denitrification.** One of the best-studied instances of deoxidation by bacteria is the process of denitrification, whereby nitrates are reduced to oxides of nitrogen, free nitrogen, and ammonia. The power possessed by many bacteria of reducing nitrates to nitrites was observed as early as 1875 (Meusel), and has been investigated by many authors since that date (Frankland, Chem. News, 1888, 57, 89; Warington, *ibid.* 1888, 57, 246; Maasen, Arbeit. K. Gesund-Amt. 1901, 18, 21; Grimbert, Ann. Inst. Past. 1899, 13, 67; Franzen and Löhmann, Zeitsch. physiol. Chem. 1909, 63, 52). The reduction to nitrite occurs in nitrate broth, is accompanied by the evolution of carbon dioxide, and, as mentioned above, is probably due to direct deoxidation, as it is effected by many bacteria which do not produce free hydrogen. The production of ammonia from nitrates is also apparently a common property of bacteria, but the relations in this case have not been so clearly established as in that of nitrite. The evolution of oxides of nitrogen from a fermenting liquid was observed by Dubrunfaut (1868), in the case of fermenting molasses; but the production of the oxides was ascribed to purely chemical causes. Since that time, however, the production of nitrous and nitric oxides from nitrites by bacteria has been frequently observed in mixed fermentations. With pure cultures the phenomenon is much less common, but an organism known as *B. denitrificans* (Stutzer and Burri), which is however probably identical with *B. pyocyaneus* (Flügge), has been described, which ordinarily reduces nitrates to nitrogen, but in presence of asparagine produces nitric oxide (Gayon and Dupetit, Compt. rend. 1882, 128, 442). Another organism, *B. nitroxus* (Bey. and Mink.), is chiefly responsible, according to Beyerinck and Minkmann (Centr. Bakt. Par. ii. 1909, 25, 30) for the almost universal occurrence of nitrous oxide in the gases produced when soil is added to nitrate broth. So vigorous is this process that a stream of gas may be obtained containing 80 p.c. of nitrous oxide, and capable of relighting a glowing splint. *B. pyocyaneus*, *B. stutzeri* (L. and N.), and *M. denitrificans* (Bey. and Mink.), all produce nitrous oxide from nitrates.

Finally, in many cases, the reducing action of bacteria on nitrates proceeds as far as the production of free nitrogen. This phenomenon, since it was first attributed to bacterial action by Gayon and Dupetit, in 1882 (Compt. rend. 1882, 95, 664), has been the subject of numerous investigations, on account of its importance in agriculture. It has been conclusively established that, in presence of suitable carbonaceous nutriment, nitrates are readily decomposed in this way by many bacteria, especially in the absence or scarcity of oxygen. Jensen has shown (Centr. Bakt. Par. ii. 1897, 3, 622; 1898, 4, 401) that in these cases the oxygen of the nitrate is utilised for the oxidation of the organic matter, and that the presence of free oxygen greatly diminishes the extent of the denitrification. It seems probable that the 'nitrogen' estimated by the older observers was really a mixture of nitrogen and nitrous oxide.

Putrefaction. The term 'putrefaction' is

usually applied to the decomposition which is set up by bacteria in animal and vegetable remains at the ordinary temperature, and which is accompanied by the production of malodorous compounds and gases. The chief source of these is the protein matter of the organism, so that the characteristic feature of putrefaction is the bacterial decomposition of proteins. The process consist chemically in a hydrolysis of the proteins into simpler molecules, followed or accompanied by the decomposition of these, yielding, according to circumstances, highly oxidised substances or a series of reduction products. In the presence of an abundant supply of oxygen, the process continues until the final products are carbon dioxide, water, ammonia, and mineral salts, whereas in a limited supply or in absence of oxygen, a whole series of compounds is formed comprising bases, acids, volatile sulphur compounds, &c.; and this is the characteristic phenomenon known as putrefaction. Similar chemical changes are produced when proteins are fused with caustic alkalis at 250° (Gautier and Étard, Compt. rend. 1882, 94, 1357).

The immediate origin of the products of putrefaction is then to be sought in the various products of hydrolysis of the proteins. These consist, as is well known, chiefly of amino acids, diamino acids, such as arginine and lysine, and a number of other compounds, among which may be mentioned as of special importance histidine, or β-iminazole-α-aminopropionic acid (α-amino-β-glyoxaline 4 (or 5)-propionic acid), tryptophane or indole-α-aminopropionic acid, and cystine $(COOH\cdot CH(NH_2)\cdot CH_2\cdot S)_2$.

The amino acids undergo decomposition in at least two different ways. In the first place, the amino group may be removed by reduction, yielding the corresponding fatty acid (equation *a*), which then either undergoes oxidation (equation *b*), yielding a lower acid or simply loses carbon dioxide (equation *c*):

(*a*) $R\cdot CH(NH_2)\cdot COOH + 2H = R\cdot CH_2\cdot COOH + NH_3$

(*b*) $R\cdot CH_2\cdot COOH + 3O = R\cdot COOH + H_2O + CO_2$

(*c*) $R\cdot CH_2\cdot COOH = R\cdot CH_3 + CO_2$.

Thus leucine $(CH_3)_2CH\cdot CH_2\cdot CH(NH_2)\cdot COOH$ yields valeric acid, and it is probable that formic, acetic, propionic, butyric, and caproic acids, which are all present in the products of putrefaction, are formed in a similar way. Of special interest are the products obtained in this way from tryptophane, a substance which was discovered by Hopkins and Cole (J. Physiol. 1902, 27, 418), among the products of hydrolysis of proteins by trypsin, and which is the mother substance of the various indole derivatives to which the characteristic odour of fæces is largely due.

Tryptophane has been found by Ellinger (Ber. 1907, 40, 3029) to be indole-α-aminopropionic acid, of the formula

$$NH\langle \begin{matrix} C_6H_4 \\ CH \end{matrix} \rangle C\cdot CH_2\cdot CH(NH_2)\cdot COOH,$$

and is decomposed by putrefaction in the manner described above, yielding successively indolepropionic acid $C_8H_6N\cdot CH_2\cdot CH_2\cdot COOH$, indoleacetic acid $C_8H_6N\cdot CH_2\cdot COOH$, and indole C_8H_7N. A certain amount of skatole or α-methylindole $NH\langle \begin{matrix} C_6H_4 \\ CH \end{matrix} \rangle C\cdot CH_3$ is also formed, probably by a reaction of the type (*c*) given above. By similar reactions phenylalanine $C_6H_5\cdot CH_2\cdot CH(NH_2)\cdot COOH$ yields successively phenylpropionic acid, phenylacetic acid, and benzoic acid, whilst tyrosine, or *p*-hydroxyphenylaminopropionic acid

$$OH\cdot C_6H_4\cdot CH_2\cdot CH(NH_2)\cdot COOH$$

is converted into *p*-hydroxyphenylpropionic acid (hydroparacumaric acid, Baumann, 1879), *p*-hydroxyphenylacetic acid (Salkowski, E. and H., Ber. 1879, 12, 648; 1880, 13, 189, 2217), *p*-cresol, *p*-hydroxybenzoic acid, and phenol. In an abundant supply of oxygen even these simple aromatic compounds are completely oxidised; thus a bacillus has been isolated which in pure culture readily oxidises dilute solutions of phenol (Fowler, Ardern, and Lockett, Proc. Roy. Soc. B, 1910, 83, 149).

Succinic acid, which is always formed in putrefaction, is probably derived from aspartic acid $COOH\cdot CH_2\cdot CH(NH_2)\cdot COOH$ by reduction (Salkowski).

It is not improbable that this type of decomposition of the amino acids may be accompanied by the type of decomposition which is brought about by yeast in presence of sugar and has already been discussed, the characteristic feature of which is that the amino group is removed with formation of a keto acid, which then undergoes further decomposition.

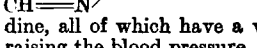
A second extremely important mode of decomposition of the amino acids, diamino acids, &c., during putrefaction, is the simple elimination of carbon dioxide, leading to the formation of bases:

(*d*) $R\cdot CH(NH_2)\cdot COOH = R\cdot CH_2\cdot NH_2 + CO_2$.

(*e*) $NH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH(NH_2)\cdot COOH$ (Lysine.) $= NH_2[CH_2]_3\cdot CH_2\cdot NH_2 + CO_2$. (Cadaverine.)

Many bases have been isolated from putrefying mixtures, and great importance is to be attached to their formation, inasmuch as several of them have a very marked physiological action. The observation that putrefying flesh may contain poisonous basic substances, liable to be confused with the vegetable alkaloids, was made by Selmi (1872), who gave to these bases of animal origin the name ptomaines (πτῶμα, a corpse), and they were then more thoroughly investigated by Brieger. It was at first thought that the poisonous products which result from the action of bacteria on various culture media and on meat, fish, &c., were also members of this class, and the effect of pathogenic bacteria on the living organism was ascribed to the production of these same substances in the system, a view to which the term 'ptomaine-poisoning,' still erroneously applied to cases of meat-poisoning, &c., gives expression. It has now, however, been found that the characteristic and specific poisons produced by bacteria are probably much more complex in their structure, and belong more probably to the class of proteins than to that of the ptomaines. They are termed toxins or bacterial toxins, and are distinguished as ectotoxins, which pass out of the bacterial cell into the surrounding medium (as do diphtheria toxin and tetanus toxin), and endotoxins, which are retained within the cell, but appear to pass out of it after death (typhoid toxin, &c.).

The origin of many of the simple mono- and di-acid bases which occur in putrefaction can

be traced to the corresponding amino acids, among these being *iso*amylamine derived from leucine, phenylethylamine derived from phenylalanine, *p*-hydroxyphenylethylamine derived from tyrosine, and *β*-iminazole ethylamine  derived from histidine, all of which have a very marked effect in raising the blood pressure, or in other ways, and are of physiological importance because they are in all probability formed in the intestine and absorbed (Barger and Walpole, J. physiol. 1909, 38, 343; Barger and Dale, *ibid.* 1910, 41, 19, 499). Of the diamino-bases isolated by Brieger may be mentioned ethylenediamine

$$NH_2 \cdot CH_2 \cdot CH_2 \cdot NH_2,$$

putrescine or tetramethylenediamine

$$NH_2 \cdot [CH_2]_4 \cdot NH_2$$

derived from arginine, cadaverine or pentamethylenediamine derived from lysine (equation *e*), as well as neuridine and saprine, isomeric with cadaverine, but of unknown constitution.

In addition to these, trimethylamine, choline $CH_2(OH) \cdot CH_2 \cdot N(CH_3)_3OH$, betaine

$$COOH \cdot CH_2 \cdot N(CH_3)_3OH,$$

muscarine $CH(OH)_2CH_2 \cdot N(CH_3)_3OH$, and neurine $CH_2 : CH \cdot N(CH_3)_3OH$, of which the last two are highly poisonous, all occur, probably derived not from proteins, but from lecithin and its allies, which yield, on hydrolysis, glycerol-phosphoric acid, fatty acids, and choline. Finally, an invariable product of the action of bacteria on proteins is ammonia, formed either by reduction of amino-acids as explained above, or by their oxidation.

The gases evolved consist of carbon dioxide, hydrogen, and sometimes methane, nitrogen, and sulphuretted hydrogen. Some of the sulphur of the proteins is converted into methylmercaptan (Nencki), and traces of many other sulphur compounds are formed, these being the main cause of the characteristic smell. The phosphorus is chiefly converted into phosphate, the evolution of phosphine alleged by some observers being doubtful.

The organisms which bring about these characteristic changes are very numerous. Usually many different organisms are present, and there seems little doubt that in some cases the various stages of decomposition are effected by different species of bacteria. Reference has already been made to the effect of the presence or absence of air, but this not only affects the chemical changes produced, but also the nature of the bacterial flora. In a free supply of air the organisms are mainly aërobic, whereas in a limited supply anaërobic organisms are chiefly present. Frequently the surface of the putrefying mass is occupied by aërobic organisms, and these use up the oxygen, and provide suitable conditions for the development of anaërobes at a lower stratum. It appears also that the primary proteins are directly attacked and digested by one group of organisms, those which produce an ecto-proteoclastic enzyme, whilst a second group possessing insoluble endo-proteoclastic enzymes, is only able to decompose the simpler products formed by this hydrolysis.

Of the actual organisms which are usually present there may be mentioned *B. putrificus* (Bienstock), perhaps the most characteristic of all, which is a sporing anaërobe; *B. vulgaris* (L. and N.) (formerly known as *proteus*), *B. fluorescens liquefaciens*, *B. mesentericus* (L. and N.), all of which attack and digest albumins. Belonging to the second group, which only decompose simpler proteins, are *B. coli communis* and its allies, the characteristic bacilli of the large intestine, many of which produce indole and indole-acetic acid, *B. prodigiosus* (Flügge), *Streptococcus pyogenes* (Rosenbach), &c. In any particular case the flora is largely conditioned by the exact nature of the putrefying material, so that meat, fish, milk, eggs, &c., all have their characteristic organisms and modes of decomposition.

Fermentations produced by Moulds.

A number of moulds, especially belonging to the families *Aspergillaceæ* and *Mucoraceæ*, are distinguished by producing definite chemical changes of a fermentative character, some of them by the secretion of soluble enzymes, and others by means of endoenzymes.

Alcoholic fermentation. The power of producing alcoholic fermentation is common to a large number of the *Mucoraceæ*, but is only possessed to any considerable extent by a single species of the *Aspergillaceæ*. *Allescheria Gayoni* (Saccardo and Sydow = *Eurotiopsis Gayoni*, Cost.) appears to be capable of producing a typical alcoholic fermentation of glucose, lævulose, maltose, and lactose, producing as much as 8 p.c. of alcohol in the medium, and forming glycerol and succinic acid in a similar manner to yeast.

The alcoholic fermentation produced by many species of *Mucor* has long been a subject of interest. When the mycelium of *M. racemosus*, (Fres.) for example, is submerged in a nutrient medium containing sugar, alcoholic fermentation occurs, and at the same time the mycelium breaks up into spherical cells, which continue to grow by budding, and have hence been termed spherical yeast. The opinion has been held at various times that these cells were true yeasts, and moreover that all yeast had a similar origin. The first statement has now been definitely disproved, and no satisfactory evidence exists in favour of the second. It was further thought that when growing in the normal manner on the surface of the liquid, the mucor had only the power of oxidising the glucose, but that when submerged and thus deprived of a free supply of air, it became able to ferment it (Pasteur). It has, however, been established by the work of Wehmer (Centr. Bakt. Par. ii. 1905, 14, 556, 15, 8) and Kostytschew (*ibid.* 1904, 13, 490) that the mould produces just as much alcohol in presence of a free supply of air as when submerged, and that the commencement of alcoholic fermentation and the production of spherical yeast cells are not causally connected. A very large number of species of *Mucor* and *Rhizopus* have been carefully examined as to their power of producing alcohol and fermenting the polysaccharides (*see* Wehmer, article in Lafar, Technisch Mykologie, iv. 517).

Production of diastase. Some species of these two families produce such large amounts of diastatic enzyme that they have been employed both industrially and domestically for

the saccharification of starch, and a considerable number, if not all of them, produce a certain amount of this enzyme.

Mucor rouxii (Calm.), Wehmer, (*Amylomyces rouxii*) was isolated by Calmette from Chinese yeast, and is employed in pure culture for converting the starch in a sterilised distillery wash into sugar, which is then fermented by a pure culture of yeast and distilled.

Aspergillus oryzæ (Ahlburg), Cohn, has long been employed in Japan for the preparation of saké from rice, and of the soya sauce from the soya bean. The diastase of this organism, known as takadiastase, acts on starch much more energetically than malt diastase.

The oxalic acid fermentation. A very remarkable instance of oxidative fermentation is afforded by *Aspergillus niger* (van Tieghem) (*Sterigmatocystis nigra*), which converts glucose into oxalic acid. When this mould is grown on a nutrient solution containing glucose at 15°–20°, free oxalic acid is produced, the acidity increases up to a maximum, and then gradually diminishes and finally disappears. If, however, calcium carbonate or an alkaline phosphate be added, the oxalic acid accumulates, either as insoluble calcium oxalate or as an acid oxalate. In this way, for example, 1·5 grams glucose yielded 1·05 gram of oxalic acid in the form of calcium oxalate, whereas in the absence of chalk the maximum amount was 0·298 gram. The complete conversion of all the carbon of the glucose into oxalic acid would yield about 2·25 grams, so that the yield is approximately 50 p.c., the remainder of the glucose being presumably used for the needs of the organism (Wehmer, Ber. Bot. 1891, 9, 223, 163; Bot. Zeit. 1891, 49, 233; Annalen, 1892, 269, 383).

The citric acid fermentation. Whereas *Aspergillus niger* produces oxalic acid from glucose, other members of the *Aspergillaceæ*, *Citromyces Pfefferianus* and *C. Glaber*, described by Wehmer; and *C. citricus*, *C. tartaricus*, and *C. oxalicus*, described by Mazé and Perrier (Compt. rend. 1904, 139, 311; Ann. Inst. Past. 1904, 18, 553), convert this sugar into citric acid. As in the case of oxalic acid, the citric acid is further oxidised if it be allowed to remain in the free state in the presence of the organisms, but accumulates when it is converted into a salt by the addition of calcium carbonate. About half the sugar can be converted into citric acid in the ratio $C_6H_{12}O_6 : C_6H_8O_7$. Buchner and Wüstenfeld (Biochem. Zeitsch. 1909, 17, 395), working with *C. citricus*, found that the maximum amount of citric acid produced amounted to 56 p.c. of the sugar. In one case, for example, in presence of calcium carbonate, the weight of the mould produced in 66 days at air temperature amounted to 0·88 gram, the total weight of sugar used being 3·5 grams, and of citric acid produced 1·95 grams. A large amount of carbon dioxide is simultaneously evolved, corresponding in various experiments to the oxidation of 48–77 p.c. of the sugar, the citric acid in the same experiments amounting to 33–38 p.c. of the sugar, and the new growth of mould to 5–31 p.c. of the sugar. The characteristic formation of citric acid could not be obtained with press juice nor with acetone preparations of the mycelium. Citric acid is also formed from glycerol and from alcohol, as well as in small quantities *in vacuó* from the mycelium of the mould alone (Mazé and Perrier).

In their action on sugar and allied compounds the moulds differ very decidedly from the bacteria. The production of lactic, acetic, butyric, and formic acids, and the evolution of hydrogen and carbon dioxide, which are characteristic of so many bacterial actions, are not observed among the moulds. On the other hand, the latter are often capable of producing alcoholic fermentation, are richly endowed with the various hydrolytic enzymes, and, in some cases, produce compounds, which, like malic, oxalic, and citric acids, are characteristic of the higher plants. Mazé and Perrier regard the citric acid as a product of catabolism of the cell substance, induced by lack of nitrogen, and not as a true product of the oxidation of sugar; whereas Buchner and Wüstenfeld ascribe its formation to a process analogous to the production of parasaccharic acid

$CH_2(OH)\cdot CH(OH)\cdot CH(OH)(COOH)\cdot CH_2\cdot CH_2(OH)$

from lactose by milk of lime (Kiliani).

Authorities.—A very copious literature now exists on the subjects of fermentation, enzyme action, and chemical action of bacteria. The chief works consulted in the preparation of the foregoing article, in addition to the original papers, are:

Lafar, Technische Mykologie (Gustav Fischer, Jena), 4 vols., vol. v. in progress.

Oppenheimer, Die Fermente und Ihre Wirkungen, 3 vols. (Leipzig, F. C. W. Vogel, 1909–10).

(Monographs on Biochemistry, Longmans, Green, & Co., London.)

Bayliss, The Nature of Enzyme Action.

Armstrong, The Simple Carbohydrates and Glucosides.

Harden, Alcoholic Fermentation.

Buchner, H. and E., and Hahn. Die Zymasegärung (Oldenbourg, Berlin, 1903).

A. H.

FERONIA GUM *v.* GUMS.

FERRATES *v.* IRON.

FERRIC ACETATE *v.* ACETIC ACID.

FERRIC SALTS *v.* IRON.

FERRITE. This term has unfortunately several different meanings. To the chemist it implies a salt in which ferric oxide plays the part of an acid, for example, barium ferrite $BaFe_2O_4$. In a mineralogical sense it was first applied by H. Vogelsang, in 1872, to an amorphous iron hydroxide, of unknown composition, which, as red and yellow particles, is present in many partially decomposed igneous rocks. In this sense the term is much used by certain petrologists for the patches of indefinite ferruginous alteration products seen under the microscope in thin sections of rocks. The same name has also been applied to ferruginous pseudomorphs after olivine occurring in the doleritic rocks of the neighbourhood of Glasgow (M. F. Heddle, Min. Mag. 1882, 1887). It has also been much used by metallographers, following H. M. Howe (The Metallurgy of Steel, 1890), for pure metallic iron, which, together with iron carbide, &c., forms one of

the microscopic constituents of iron and steel. L. J. S.

FERRITE (v. *supra*) the name given to the carbon-free constituent of steels. Usually it is nearly pure iron, but in special steels it may be an alloy of iron with silicon, chromium, tungsten, &c. Ferrite exists in three forms: α-iron, stable up to 760°; β-iron, stable between 760° and 900°; and γ-iron, stable above 900°. Of these, γ-iron is the hardest (Howe, Metallographist, 1898, i. 259). The freezing-point of ferrite is 1505° (Carpenter, J. Iron and Steel Institute, 1908, iii. 290; Saklatwalla, *ibid.* ii. 92).

Under the microscope ferrite is characterised by its softness, and the cubic structure revealed by deep etching with acids or cupric ammonium chloride (Andrews, Engineering, 1895, 88; Stead, J. Iron and Steel Institute, 1898, i. 145).

FERROCHROME, FERROMANGANESE, FERROSILICON, FERROTITANIUM, FERROTUNGSTEN, FERROVANADIUM *v.* IRON.

FERROCYANIDES *v.* CYANIDES.

FERROTYPE *v.* PHOTOGRAPHY.

FERROUS ACETATE *v.* ACETIC ACID.

FERTILISERS or MANURES. Either of these terms might properly be applied to any material added to the soil for the purpose of increasing its fertility, and, in this sense, would be extended to include lime, chalk, marl, and even clay and sand. In common practice, however, the term 'manure' or 'fertiliser' is restricted to materials the main function of which is to convey directly to the soil some constituent or constituents of plant food, to the exclusion of those of which the fertilising action is mainly indirect, consisting in the improvement of the physical condition of the soil or the development of its inherent or natural chemical resources. The chief constituents of plant food which are naturally taken up from the soil are nitrogen, phosphorus, sulphur, potassium, calcium, magnesium, and iron, together with the less important constituents silicon, chlorine, and sodium. A manure or fertiliser, in the sense in which the term is ordinarily used, will always contain one or more of these substances.

Apart from calcium—the supply of which is necessary in special cases only—nitrogen, phosphorus, and potassium are by far the most important constituents to be applied as manure, as they are those in which the soil is most generally deficient.

In an efficient fertiliser the constituents must be in a condition suitable for immediate assimilation by the plant, or must be capable of speedily acquiring this condition after mixing with the soil. Manures or fertilisers are sometimes classified as 'natural' and 'artificial,' but the dividing line is not always easily drawn. In the present article we shall briefly consider the principal substances employed as manures or fertilisers, passing on to some observations as to the general relative utility of some of them, and shall then refer to the special methods employed for their analysis.

Farmyard manure. Farmyard manure and stable manure are composed of litter mixed with the excreta of animals. The litter in farmyards is usually straw, but this has been to a large and increasing extent superseded in stables by dried and shredded peat moss. In some parts of the country bracken is used for litter, and in hop districts hop-bine is thus worked up into manure. The composition of the manure depends initially to some extent on the nature of the litter, but to a greater extent on the length of time the litter has been in use, the number and kind of animals littered on it, and the quantity and quality of the food consumed by them. Its final value—that is to say, its value at the time of its application to the land—is also largely governed by the mode of 'making,' and the mode and duration of storage. Its valuable effect on the soil may be said to be twofold. In virtue of the large quantity of bulky organic or carbonaceous matter that it contains, it improves the physical condition of the soil, making 'heavy' soils more 'open,' and 'light' soils more retentive. At the same time, it returns to the land the mineral matter and much of the nitrogen previously removed from it in the form of straw, as well as much of the nitrogen and most of the phosphoric acid and potash derived from home-grown fodder consumed during its production, reinforced by similar matter derived from the simultaneous consumption of additional purchased food.

The proportion of the nitrogen and manurially available 'mineral' matters absorbed and retained by animals from their food depends upon their age, condition, and other circumstances. Thus, a young growing steer, or a cow in milk, will assimilate more nitrogen and phosphates, and consequently void less in the form of fæces and urine, than will a fattening ox, which has already built up its frame and principal nitrogenous tissues, and is increasing its weight mainly by the production of fat. Thus the quantity of nitrogen voided in fæces and urine might vary from more than 95 p.c. of the nitrogen consumed in the food to as little as 75 p.c. The proportion of phosphoric acid and potash voided will be greater. Obviously, in the case of horses, which only spend a portion of their time in the stable, only a fraction of the excreta will be mingled with the litter; and so also in the case of cattle which are turned out for a part of their time. It is manifestly only the stall-fed or yard-fed animal which contributes the whole of the nitrogen, phosphates, and potash which it voids to the actual manure heap.

Unfortunately for the farmer, the fertilising matter thus initially contributed to the manure is by no means all ultimately available for utilisation. Continual losses occur. These are at their highest in an open farmyard exposed to the weather, where more or less loss of the valuable soluble constituents of the manure is always going on by mere drainage, and where there is the greatest facility for the evaporation of ammonia. They are at their lowest where the animals are fed in close boxes, in which the litter is trodden down compactly in watertight pits; but even here there is constant loss by reason of fermentative action, not only through evaporation of ammonia, but also by the reduction of ammonia and other easily decomposable nitrogenous compounds into free nitrogen. The

losses that thus occur have been studied by numerous investigators, including Lawes and Gilbert, A. Voelcker, J. A. Voelcker, Hall, Maercker, and Schneidewind, Holdefleiss, Müntz and Girard, Wood, Russell, and numerous others. The general result has been to show that, even under the best conditions of ordinary production, the loss of nitrogen may be expected to amount to about 15 p.c. by the time the manure is taken out of the boxes, while in shallow stalls or yards it may amount to 30 or 40 p.c. Further loss of nitrogen takes place after the manure is heaped or stacked for 'ripening,' or for preservation until it is convenient to transfer it to the land. It is probable that, even with fairly good management, the ultimate loss of nitrogen may amount on the average to 50 p.c. of the initial quantity. Under bad management, especially with open yards and free drainage, it is probably often much greater.

Various plans have been adopted or suggested for checking the loss, such as the use of gypsum or superphosphate sprinkled in the manure during its accumulation, to absorb ammonia; or of kainit, which checks fermentation. In any case the manure should be heaped as compactly as possible, with layers of earth in it, and the heap should be covered with earth. It has been demonstrated that the greatest percentage loss of nitrogen unfortunately occurs in the manure that is initially richest, namely, that produced by animals liberally fed on highly nitrogenous food.

It is obviously difficult to give an average composition for so variable a substance as farmyard manure, but broadly it may be said to consist of:

Water	about 75 p.c.
Organic and volatile matter .	„ 22 „
Mineral matter (exclusive of earth)	„ 2½–3 „

But, as the water may vary from perhaps as little as 65 p.c. to over 80 p.c., the quantity of organic matter is liable to considerable inverse variation. The proportion of nitrogen is usually from about 0·45 to 0·65 p.c., that of potash from about 0·4 to 0·8 p.c., and that of phosphoric acid from about 0·2 to about 0·4 p.c.

Hall gives the following tables illustrating the general composition of farmyard manure, and also showing the influence of feeding on the nitrogen contents of the manure:—

COMPOSITION OF FARMYARD MANURE FROM VARIOUS SOURCES (HALL).

—	Water	Nitrogen	Phosphoric acid	Potash
	p.c.	p.c.	p.c.	p.c.
1. Fresh long straw manure	66·17	0·544	0·318	0·673
2. No. 1 after rotting .	75·4	0·597	0·454	0·491
3. Very old and short, from a mushroom bed .	53·14	0·80	0·63	0·67
4. Fresh } French data . {	75·0	0·39	0·18	0·45
5. Rotten } French data . {	75·0	0·50	0·26	0·53
6. Very old } French data . {	79·0	0·58	0·30	0·50
7. Rothamsted average .	76·0	0·64	0·23	0·32
8. Fresh liquid manure .	98·02	0·044	0·051	0·355
9. Old ditto . . .	99·13	0·026	0·014	0·22

PERCENTAGE COMPOSITION OF FARMYARD MANURE (HALL).

Diet	Year	Dry matter	Total nitrogen	Nitrogen as ammonia	Nitrogen as amides	Insoluble nitrogen	
Roots and hay only	1904	23·6	0·577	0·046	0·067	0·464	Made into mixen & stored
Cake-fed	1904	24·03	0·716	0·079	0·096	0·541	
Roots and hay only	1905	29·5	0·462	0·040	0·047	0·375	Do.
Cake-fed	1905	31·3	0·698	0·182	0·055	0·461	
Roots and hay only	1906	22·0	0·466	0·022	0·033	0·411	Do.
Cake-fed	1906	24·3	0·690	0·097	0·049	0·544	
Roots and hay only	1907	25·3	0·589	0·125	0·053	0·411	Not stored
Cake-fed	1907	25·5	0·815	0·377	0·033	0·405	

Straw manure will contain more potash than peat moss manure, but the latter contains more nitrogen. Stable manure is 'hotter'—that is to say, ferments more rapidly—than farmyard manure proper. Very large quantities are purchased from town stables by market gardeners and other farmers within easy carriage of cities. This largely consists of litter that a farmer would regard as only half used, owing to the necessity for the prompt clearing of town stables; and it is necessarily poor in soluble nitrogen compared with farmyard manure. The following analyses by Dyer (tabulated by Hall) illustrate the composition of specimens of such manure, made both with straw and with peat moss, fresh and after some months' storage in heap on the farm of the purchaser:—

COMPOSITION OF LONDON STABLE MANURE (DYER—TABULATED BY HALL).

—	From peat moss	From straw	From mixed peat moss and straw				
			Fresh		After storage		
			1	2	1	2	3
Water . .	77·80	70·0	76·1	62·0	53·8	61·9	52·9
Organic matter	18·00	24·3	19·3	26·4	17·5	22·0	23·0
Nitrogen, sol.	0·51	0·52	0·08	0·08	0·06	0·08	0·10
„ insol.	0·37	0·10	0·46	0·62	0·58	0·68	0·79
Phosphoric acid	0·37	0·48	0·33	0·45	0·49	0·56	0·66
Potash . .	1·02	0·59	0·45	0·58	0·58	0·65	0·80

In addition to its 'mineral' constituents (phosphates, potash salts, &c.), well-made farmyard manure contains enough available nitrogen in the form of ammonia compounds and easily nitrifiable organic matters to enable it to begin to act as plant food immediately; while it has at the same time a reserve of insoluble matter, partially decomposed organic matter which yields up nitrogen more slowly and gradually, the effect of much of which is realised only in subsequent seasons.

The duration of the action of farmyard manure largely depends upon the nature of the soil. In some 'open,' 'hot,' gravelly soils, farmyard manure is used up with remarkable rapidity. On other soils, its action may be spread over a considerable number of years; but in such cases its fertilising effect, especially on arable land, diminishes to an increasing

extent each year, until, under the circumstances of ordinary farming, it becomes imperceptible. There are, however, experimental plots at Rothamsted, where, under circumstances peculiarly favourable to its operation, the effects of early dressings of farmyard manure are still evident after the lapse of 40 or 50 years.

The valuation of the unexhausted effect of farmyard manure in relation to the feeding stuffs consumed in producing it, is an important matter in the application of the Agricultural Holdings Act. This subject is fully discussed by Hall and Voelcker in a paper 'On the Valuation of the Unexhausted Manure obtained by the Consumption of Foods by Stock,' in the Journal of the Royal Agricultural Society of England, 1902, vol. 63 (also republished as a separate pamphlet by John Murray, of Albemarle Street, London, W.). In this paper the original valuation tables of Lawes and Gilbert have been revised in the light of later investigation, and, as thus revised, have been adopted by the Central and Associated Chambers of Agriculture.

The general chemistry of farmyard manure has been well treated in Warington's Chemistry of the Farm (Vinton), and more recently and fully by Hall in his work on Fertilisers and Manures (Murray).

Peruvian guano. Guano was originally introduced into England from Peru in 1839, and for many years it occupied the first place among concentrated fertilisers. The original rich deposits have been for a long time exhausted, but considerable importations of Peruvian guano are still made, chiefly from recent deposits. Guano is formed from the excrement and carcases of sea-fowl. The fresh excrements are highly nitrogenous, and consist chiefly of uric acid and calcium phosphate. If the climate is hot and dry, the excrements are quickly desiccated and the nitrogenous matter protected. These conditions exist on the rainless coast of Peru. In a moist climate the nitrogenous matter is quickly converted into ammonia and dissipated by evaporation or drainage, a phosphatic guano practically destitute of nitrogen remaining. The main supply of Peruvian guano for 30 years was from the Chincha Islands, which yielded, in all, from what we may call the original deposits, about 10,000,000 tons. This guano was a dry, excellent fertiliser, containing from 13 to 14 p.c. of nitrogen, and from 13 to 14 p.c. of phosphoric acid. On its exhaustion, about the year 1868, guano was shipped from the Guanape and Macabi Islands. This was a damp guano containing from 9 to 11 p.c. of nitrogen, and about 12–14 p.c. of phosphoric acid. This was succeeded by importations, still from old deposits, from the Ballestas Islands and the islands of Lobos de Afuera, and deposits on the mainland at Pabellon de Pica, Punta de Lobos, and Huanillos. Many of these deposits were of low nitrogenous content, but very rich in phosphates, while some possessed very much the character of the original Chincha guano. In more recent years shipments have been coming in from new deposits formed on the original islands, which have again become 'guaniferous,' the birds being now specially preserved with a view to the constant renewal of the deposits and the consequent maintenance of the output. These deposits of fresh guano are highly nitrogenous, and would be much richer in percentage composition but for the fact that a good deal of sand is sometimes unavoidably mixed with them.

The nitrogen in Peruvian guano is partly in the form of ammonia salts and partly in organic combination; and in some cases small quantities of nitrate are also present. The main part of the phosphoric acid is in the form of finely divided calcium phosphate, some of the phosphoric acid also being in combination with ammonium, sodium, or potassium. Some of the phosphoric acid, therefore, is immediately soluble in water, while even that which is insoluble is readily attacked by weak acids and rapidly available as plant food. There is also present an appreciable quantity of potash salts. Guano is, therefore, an extremely valuable manure, and has always commanded relatively higher prices than most other concentrated fertilisers. Having regard to the great variation in the composition of different cargoes, it has been for many years the practice of the chief importers to prepare a mixed or 'equalised' Peruvian guano, containing a fixed percentage of nitrogen, for the sake of those users who wish for guano of constant composition; but the guano is also on sale in its unmixed or natural condition, at prices varying *pro rata* with its composition. It may be added that dissolved Peruvian guano, which was introduced by Messrs. Ohlendorff in 1864, and is still manufactured by their successors, the Anglo-Continental Guano Works, is Peruvian guano treated with sulphuric acid to fix the ammonia and render the phosphate nearly all soluble in water. It is a large article of manufacture, and is sold containing definite percentages of nitrogen and soluble phosphate.

Examples of analyses of recently imported cargoes of Peruvian guano of different grades from several of the islands are given on p. 540.

Besides Peruvian guano, the only other nitrogenous bird guanos of commercial importance have been obtained from Patagonia and from the Ichaboe Islands off the coast of Africa. Ichaboe guano, being from fresh deposits, is rich in nitrogen, of which it contains from 9 to 14 p.c. Its general composition is similar to that of Peruvian guano of similar grade. An appreciable proportion of the nitrogen, however, is in the form of feathers.

Seaweed. This is largely used in some localities near the sea. When quite fresh, seaweed contains about 80 p.c. of water. Its composition varies a good deal. The nitrogen may be 1–3 p.c. of the dry matter. The average percentage of potash in 20 analyses of *Fucus* and *Laminaria* was 3 p.c., and of phosphoric acid 0·5 p.c. of the dry matter. The proportion of nitrogen and potash in fresh seaweed is thus very similar to that in farmyard manure, while the phosphoric acid is deficient.

Fish manure or fish guano. Whole fish are employed as manure in places near the sea. Way found in fresh sprats 63·7 p.c. water, 1·94 p.c. nitrogen, and 2·1 p.c. ash, including 0·43 potash and 0·90 phosphoric acid.

Fish manure, or 'fish guano,' as it is called, is made on a considerable scale from various kinds of fish refuse. The Norwegian fish guano

—	Ballestas	Lobos d'Afuera	Cantores	Lobos de Tierra	South Guanape	North Guanape	Lobos d'Afuera		
Moisture . . .	18·06	18·30	28·74	24·44	25·72	16·60	15·20	15·58	10·44
Organic matter and ammonium salts . .	40·36	36·32	35·66	32·16	29·91	29·50	26·55	19·57	11·96
*Phosphoric acid . .	9·74	10·62	13·25	11·84	14·79	16·35	15·07	17·21	19·13
Lime . . .	9·21	10·53	11·45	10·75	12·25	13·08	12·46	14·17	14·50
†Magnesia, alkalis, &c.	7·93	9·61	9·10	8·64	9·84	11·92	10·65	11·27	12·32
Silicious matter . .	14·70	14·62	1·80	12·17	7·49	12·55	20·07	22·20	31·65
	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00
Total nitrogen . .	11·43	9·97	9·44	8·32	7·19	7·07	6·80	4·58	2·58
Equal to ammonia .	13·88	12·11	11·46	10·10	8·73	8·58	8·26	5·56	3·13
*Equal to tricalcium phosphate . .	21·28	23·20	28·95	25·87	32·32	35·72	32·93	37·60	41·80
†Including potash .	2·68	2·39	2·76	2·50	2·87	3·09	2·33	2·15	1·86

is prepared from cod. Herrings, sprats, menhadden, and other oily fish are boiled and pressed for the sake of their oil, and the residue is dried, powdered, and sold as fish guano. This manufacture is carried on in various places on the east coast of England and Scotland. It is also carried on to a large extent in London, the raw material being the fish offal of the metropolis, which, for the most part, is simply dried and ground. The principal value of fish guano lies in its nitrogen, which may vary from as little as 6 or 7 p.c. to as much as 10 or 11 p.c., according to the particular kind of fish or fish offal from which it is made, and the presence or absence of much salt or other impurities. There is also a good deal of calcium phosphate, which usually varies inversely with the nitrogen, and may range from as little as 6 or 7 p.c. up to 18 or 20 p.c. The potash is inconsiderable. The following analyses represent different qualities of fish guano :—

Analyses of Fish Guano.

Moisture . .	14·18	8·78	14·42	11·18
*Organic matter .	54·07	63·92	63·68	67·22
†Phosphoric acid .	5·58	7·35	7·50	7·72
Lime . . .	6·16	10·47	8·06	8·34
Salt, magnesia, potash, &c. .	17·31	7·03	5·54	5·14
Sand . . .	2·70	1·95	0·80	0·40
	100·00	100·00	100·00	100·00
*Containing nitrogen	6·27	8·74	9·62	10·42
Equal to ammonia	7·61	10·61	11·68	12·65
†Calcium phosphate	12·19	17·15	16·39	16·87

The practical value of the manure depends to some extent on the quantity of oil present, the smaller the quantity of oil the more readily does the manure decompose in the soil.

Phosphatic guanos. The ancient deposits of guano occurring in climates in which rain is frequent have lost almost the whole of their nitrogenous matter; they are, when free from sand or rock, of value as phosphatic manures, but have been chiefly used for the manufacture of high-class superphosphates. Some of these guanos have been considerably altered by the action of water and other natural chemical agents. One common result of this action is the formation of 'crusts,' consisting largely of calcium phosphate containing considerably less calcium than tricalcium phosphate, and therefore of special value as manure. Gypsum is also present in some cases to a considerable extent.

The principal places from which phosphatic guanos have been obtained are various islands in the West Indies and in the Pacific Ocean. Those which more particularly retained some of the distinctive characters of guanos are now for the most part used up. More deposits are still occasionally discovered, but in many cases these deposits have become so metamorphosed that they have almost passed the border line between 'guano' and 'mineral phosphate,' which is sometimes not easily drawn. At all events, their function is not that of manure, but of a raw material for its manufacture, and for practical purposes they may be placed with mineral phosphates, to be considered presently.

Ammonium sulphate (commercially called sulphate of ammonia) usually contains from about 95 to 97 p.c. of the pure salt, containing 20–20·5 p.c. of nitrogen, equivalent to from 24 to 25 p.c. of ammonia.

Sodium nitrate (commercially called nitrate of soda) is refined from the crude native deposits (known as caliche), found in the rainless areas of Chile. Good commercial sodium nitrate contains about 95 p.c. of sodium nitrate or 15·6 p.c. of nitrogen (equivalent to 19 p.c. of ammonium). The impurities are moisture, sodium chloride, sodium and magnesium sulphates, small quantities of iodates and sometimes of potassium perchlorate, while in some makes sodium nitrate is partially replaced by potassium nitrate.

Potassium nitrate, or saltpetre, is sometimes used as a source of both nitrogen and potash, but chiefly in India, where it is a native product.

Calcium nitrate has recently been introduced as a fertiliser. Its chief interest at present lies in the fact that it is manufactured from nitric acid produced from the direct combination of atmospheric nitrogen and oxygen in the flaming electric arc. Its production is said to be already considerable, but from an economical standpoint it will assume larger importance in the future, when the present abundant sources of naturally formed nitrate come to an end. As put on the market at present, it contains about 13 p.c. of

nitrogen (equivalent to about 15·8 p.c. of ammonium). Its chief fault in its present form is its extreme deliquescence, which makes it necessary to sow it directly the air-tight drums in which it is sent out are opened.

Calcium cyanamide is also a fertiliser made from the nitrogen of atmospheric air: which is passed through coarsely ground heated calcium carbide. The resulting mass contains a large proportion of calcium cyanamide, and contains about 18–20 p.c. of nitrogen. In moist earth it decomposes, yielding ammonia, according to the reaction $CaCN_2+3H_2O=2NH_3+CaCO_3$; but it is probable that other influences than mere moisture—connected probably with the microbic life of the soil—play a part in the production of ammonia. As calcium carbide is a product of the electric furnace, calcium cyanamide, like calcium nitrate, needs electric power for its production. For its manufacture *v.* NITROGEN, ATMOSPHERIC, UTILIZATION OF. It is put on the market under the name of 'kalk-stickstoff' on the Continent, or 'nitrolim' in England.

Oilcakes. Cheap or damaged oilcakes, or cakes unfit for food (as castor), are employed to a considerable extent as manure, and more particularly the residual meals obtained as by-products in the extraction of oil by spirituous solvents from rape seed, castor-oil seed, and numerous other oil seeds. They are in large request for hop manuring, and for general use on light soils, on which the farmer prefers a less rapidly active form of nitrogen than is furnished by guano, sodium nitrate, or ammonium sulphate. They will contain 4–7 p.c. of nitrogen, 1·5–3·0 p.c. phosphoric anhydride, and 1–2 p.c. potash.

Hoof and horn. The powdered horn obtained in making combs and other articles is used to a considerable extent by manure manufacturers; it is extremely rich in nitrogen, containing about 15 p.c.

Dried blood. This is a very valuable manure, its nitrogenous matter becoming readily available to the crop after mixing with the soil. Perfectly dry blood will contain about 15 p.c. nitrogen and 4 p.c. ash, of which one-half is common salt. The commercial article contains from about 11 p.c. to about 13 p.c. of nitrogen. It is in growing demand for direct application to the soil, but the greater part both of the dried blood manufactured here and of that imported from South America is purchased by the manure makers and incorporated in compound fertilisers.

Meat meal, meat guano. The residue from the manufacture of meat extract is exported as manure from South America, and from Queensland and New Zealand. The composition varies much, chiefly according to the proportion of bone ground up with the meat. The nitrogenous samples may contain 11–13 p.c. nitrogen, and 0·6–3·0 p.c. phosphoric anhydride. The phosphatic samples may contain 6–7 p.c. nitrogen, and 14–17 p.c. phosphoric anhydride.

Shoddy and wool waste. These are useful nitrogenous manures, but much less active than those previously enumerated, being only slowly decomposed in the soil. They are less used than formerly, except for hops and market gardening, owing to the cheapness of ammonium salts. Pure dry wool and hair would contain about 17 p.c. nitrogen, and 2 p.c. ash. The percentage of nitrogen in ordinary shoddy varies from 5 to 8, the general average being about 7. Shoddy is apt to contain a good deal of water; the other impurities are cotton, oil, and mineral dust.

Leather. The percentage of nitrogen is 4–6. This is the least active form of nitrogenous matter used as manure; but there are various manufacturing processes—such as treatment with acids or with steam under high pressure—whereby the character of the leather as such is more or less destroyed, the result being a fine powder capable of undergoing more rapid decomposition, and having, in some cases, a large proportion of actually soluble nitrogen.

Soot. House soot is used by farmers as a top dressing for spring corn. Good soot contains about 4 p.c. of nitrogen or nearly 5 p.c. of ammonia (say 20 p.c. of ammonium sulphate), in which form the nitrogen largely exists, but it often contains an admixture of ashes, and consequently varies a good deal.

Bones. These are seldom used in their fresh state; they have generally been first steamed to extract the fat. A more perfect method of extracting the fat by means of benzene has been introduced (J. Soc. Chem. Ind. 1884, 375, 490, 575), but not much employed. Less nitrogenous matter is removed from the bone when benzene is used. A third form of bone is that left after extracting the greater part of the gelatinous matter by boiling under pressure. The following analyses illustrate the composition of bone manures:—

BONE MEAL.

	English (containing cartilaginous matter)	English (ordinary)	Indian	Boiled or lightly steamed	Steamed or de-gelatinised
Moisture	8·24	8·80	8·48	8·62	13·52
*Organic matter	36·14	34·94	30·56	20·74	9·88
†Phosphoric acid	20·75	21·66	24·19	26·44	30·11
Lime	27·94	28·53	32·03	35·95	40·04
Magnesia, carbonic acid, &c.	5·18	4·62	4·19	7·25	5·45
Silicious matter	1·75	1·45	0·55	1·00	1·00
	100·00	100·00	100·00	100·00	100·00
*Containing nitrogen	4·72	4·19	4·01	2·33	0·91
Equal to ammonia	5·73	5·09	4·87	2·83	1·11
†Equal to tricalcium phosphate	45·34	47·33	52·85	57·77	65·79

Bones are either applied to the land directly as crushed bones, or as bone-dust or bone-flour; or they are employed for the manufacture of 'dissolved bone.' The soft parts of bone are more nitrogenous than the hard parts. Bone-flour is a fine powder, prepared from highly steamed bones.

Bone ash. This is imported from South America. It was formerly much used for preparing high-class superphosphates, but is now less employed, owing to the abundance of cheaper phosphates. Pure or bone ash will contain nearly 40 p.c. phosphoric acid. The commercial

article is usually sold on a basis of 75 p.c. tricalcium phosphate.

Basic slag. By the process patented by Thomas (1877–79), the phosphorus is removed from pig-iron. The melted iron is placed in a Bessemer converter lined with lime, a large dose of lime is added, and the blast applied. At the high temperature reached, the impurities in the iron are oxidised by the air introduced, the phosphorus becomes phosphorus pentoxide and unites with the lime. A slag is formed containing about 40–50 p.c. lime, varying quantities of magnesia, alumina, iron oxide, manganese oxide, silica, and phosphoric acid equivalent to from 20 to 50 p.c. of tricalcium phosphate. The process has been adopted to a very large extent, and basic slag is now an important product of the iron and steel industry. It has been estimated that at the present time (1910) 300,000 tons are annually produced in Great Britain alone, and the continental production is very heavy.

For several years, however, the slag was regarded as valueless, the large amount of iron present leading agricultural chemists to believe that the phosphoric anhydride would not prove available to plants, while the ferrous oxide would probably be injurious. It is now known that the phosphoric anhydride in the slag is almost wholly combined with calcium, and that this calcium phosphate is easily disintegrated and rendered soluble in the soil, and that no ill effects arise from the presence of the ferrous oxide. Tetracalcium phosphate has been regarded as the combination in which most of the phosphorus occurs (Hilgenstock, Dingl. poly. J. 250, 330; Otto, Zeitsch. Chem. 11, 255; Bücking u. Zinck, Stahl u. Eisen, 7, 245); but it is probable that the phosphate has more nearly the composition $(CaO)_5,P_2O_5,SiO_2$ (Hall). About 1·5 p.c. of the total phosphorus exists as iron phosphide, which is changed into phosphate in the soil (Jensch, Zeitsch. Chem. 10, 820). The phosphate in the slag is not soluble in water; it is dissolved to a considerable extent by a solution of ammonium citrate, and when the slag is finely ground about 80 p.c. of it should dissolve in a 2 p.c. solution of citric acid.

At first attempts were made to dissolve the phosphates in the slag, and then reprecipitate them for use as manure; this was afterwards found to be unnecessary. Field experiments with finely ground untreated slag commenced in 1882, and soon became very numerous, as it was found to produce an excellent effect. The Germans were the first to realise the importance of the new manure, and they succeeded in purchasing a large proportion of the English make before Englishmen had become alive to its value.

To be effective the slag must be very finely ground; at least 80 p.c. of it should pass through a sieve having 100 meshes to the linear inch. The grinding requires special machinery. It is advisable, according to Horn (J. Soc. Chem. Ind. 1886, 242), to break first under stamps, to further reduce between rollers, then to separate pieces of iron by passing over slanting sieves, and finally to grind between millstones.

According to Wagner's trials, 2 parts of phosphoric acid in powdered slag (of which 80 p.c. passed a sieve with meshes 0·2 mm. diameter) are equal in manuring power to 1 part of soluble phosphoric acid in superphosphate; the effect will, however, vary in different soils.

Basic slag is especially valuable on moorland soils rich in organic matter and on clay soils deficient in lime on which the continuous use of superphosphate is undesirable. It has proved especially valuable on pastureland.

Precipitated phosphate. Phosphatic minerals which are unsuitable for the manufacture of superphosphate, either from their poverty in phosphate or from the presence of an objectionable amount of iron oxide or alumina, are sometimes treated with acid, the calcium phosphate dissolved out, and then recovered by precipitation. If the addition of the neutralising base is stopped while the solution is still acid, the precipitate will consist chiefly of dicalcium phosphate.

The phosphoric anhydride in precipitated phosphate stands next in value to that existing as *monocalcium* phosphate. Commercial dicalcium phosphate may contain as much as 40 p.c. P_2O_5; it is thus a very concentrated manure, and especially suitable for use where manure must be conveyed a long distance. Owing to the introduction of basic slag, however, it is now scarcely worth while to manufacture precipitated phosphate except as a by-product. It is thus prepared incidentally to the manufacture of gelatin from bones. The bones are treated with cold hydrochloric acid, which dissolves out the phosphate, leaving the chondrin or gelatinoid matter undissolved. The phosphate is then recovered from the acid solution by precipitation with milk of lime.

Superphosphate. The phosphates previously mentioned may be applied directly to the soil with good effect, if in the condition of fine powder. Natural mineral phosphatic deposits are, however, too hard and insoluble to be economically used in this manner; these are treated with sulphuric acid, and converted into superphosphates.

The treatment of bone with sulphuric acid was originally recommended by Liebig. The treatment of mineral phosphates with sulphuric acid originated with Lawes, who took out a patent for this process in 1842, and founded a manufacture which has since reached enormous dimensions.

Superphosphate in the United Kingdom is always sold on the basis of its percentage of what is called 'soluble phosphate.' This means the quantity of tricalcium phosphate which has been rendered soluble. The phosphoric acid (P_2O_5) soluble in water is determined and calculated into its equivalent percentage of $Ca_3P_2O_8$, this being called 'soluble phosphate.' On the continent of Europe the solubility is, on the other hand, calculated as 'soluble phosphoric acid,' *i.e.* P_2O_5 dissolved by water. The method of determination will be described later on.

Phosphatic Materials used.

Superphosphate was prepared by Lawes in the first instance from spent animal charcoal; Suffolk (Tertiary) coprolite and Estremadura phosphorite were also early employed. The Suffolk coprolite was for 15 years the principal material made use of. The far superior Cambridge (Greensand) coprolite then became for

many years the chief material, but is now scarcely, if ever, used, other phosphates being much cheaper. Deposits rich in calcium phosphate have been found all over the world; many of these have been exhausted, and others given up as of inferior quality, or as being at present prices too expensive to work. We shall give some account both of some of those which have become matters of history, or the use of which is at present in abeyance from the effect of competition, as well as of those which are at present in use. The estimates given of the quantities of the various phosphates recently mined or raised are taken from a paper read at the International Congress of Applied Chemistry, in 1909, by Hermann Voss, who estimated the total output of raw phosphate in 1908 at the enormous quantity of 4,824,000 tons. This would represent in all something like 8½ million tons of superphosphate.

South Carolina or Charleston phosphate. This is apparently a converted Eocene marl. It occurs in rough masses, largely perforated by boring mollusca, and associated with fossil bones and teeth. It is classed as 'land' and 'river' phosphate; the latter is obtained by dredging the Bull, Coosaw, and Stono rivers. This phosphate came first into use in 1867, and soon became the chief material for the manufacture of superphosphate. The quantity exported to the United Kingdom in 1887 was 165,275 tons (principally river phosphate); in the same year 430,549 tons were used in the United States. There are three grades, containing phosphoric acid equal to 50–52, 55–56, and 58–60 p.c. tricalcium phosphate; they differ simply in the proportion of silicious matter present. South Carolina phosphate, though not rich enough for the preparation of high-class superphosphates, is an admirable material for the production of an ordinary superphosphate, containing, according to the quality of the phosphate used, from 11 to 14 p.c. soluble phosphoric acid, or, in commercial language, 24–30 p.c. soluble phosphate. Owing to the discovery of other deposits and to the local demand for this particular phosphate in the United States, it has at present practically ceased to be imported into England. The quantity of phosphate raised in 1908 in South Carolina and Tennessee is estimated by Voss at 800,000 tons.

Belgian and Somme phosphate. In the north of France (departments Somme and Pas de Calais) and in the adjoining districts of Belgium there exists an enormous deposit of a friable phosphatic rock, 'craie grise,' extending over seven million acres. This deposit lies on ordinary white chalk; it consists of yellowish grains embedded in a chalky matrix. The rock contains 20–30 p.c. of calcium phosphate, occurring in the crystalline grains above mentioned. In the upper layer of this deposit are pockets, chiefly developed in France, which contain a sand far richer in phosphate and poorer in carbonate than the underlying rock, the proportion of phosphate in this sand being 50–80 p.c. The sand has probably been formed from the original rock by the action of water. This phosphatic sand is known as 'Somme phosphate.'

The Belgian phosphatic rock is generally of low quality. By washing and blowing, a material containing 40–45 p.c. calcium phosphate is produced. Many schemes have been tried for removing the calcium carbonate, and thus raising the value of the material; none has yet become a commercial success. Belgian phosphate is used with other phosphates as a diluent; the carbonate it contains produces much gypsum when acted on by the sulphuric acid, and considerably improves the porosity and dryness of the manure. The export from Belgium to the United Kingdom is considerable.

One practical advantage possessed by the Belgian and Somme phosphates is that they require no grinding. Somme phosphate as imported goes entirely through a sieve of 60 wires to the inch. The output of Belgian phosphate in 1908 was estimated at 150,000 tons, and of Somme and other French phosphate at 350,000 tons.

Phosphorites. Large deposits of apatite, or of phosphates having an apatite character, occur in many places; those most worked have been the Estremadura, the Canadian, and the Norwegian. These, however, are not now brought to this country, and have for the present ceased to be worked.

1. *Estremadura phosphorite.*—An immense deposit occurs at Caceres. In composition it is a fluor-apatite, but mixed with much quartz, and with more or less calcium carbonate. There are three qualities, containing about 50, 60, and 70 p.c. tricalcium phosphate. The calcium carbonate varies from 6 to 16 p.c. The exports were in former years very large, amounting sometimes to 60,000 tons per annum.

2. *Canadian phosphorite.*—This is much richer than the Estremadura phosphorite, containing 70–80 p.c. tricalcium phosphate. The lower qualities contain much mica. The amount formerly exported to the United Kingdom was considerable.

Caribbean phosphates. Under this head we group the rock phosphates found on many of the West India Islands, some of which are often classed as phosphatic guanos.

1. *Aruba.*—This is one of the Dutch islands. The phosphate is of high quality, containing 75–80 p.c. tricalcium phosphate, but the imports now are small. The total quantity raised in 1908 is estimated at 30,000 tons.

2. *Curaçao.*—Another Dutch island. This is one of the finest phosphates available, containing about 85 p.c. tricalcium phosphate. With this phosphate, superphosphate may be made containing 44–45 p.c. soluble phosphate (20–20½ p.c. soluble P_2O_5). This deposit is not at present worked, or is, at all events, not exported to England.

3. *Sombrero.*—This valuable deposit is nearly exhausted. It contains 70–78 p.c. tricalcium phosphate.

4. *Monk and St. Martin's Islands.*—Both deposits are now exhausted; the former was of very high quality.

5. *Navassa.*—The deposit on this island has a well-marked pisolitic structure. The phosphoric anhydride is equivalent to 60–70 p.c. tricalcium phosphate. The use of Navassa phosphate is limited by the considerable amount of alumina and ferric oxide present, which makes it unsuitable for the preparation of high-class superphosphates.

6. *Redonda and Alta Vela.*—The phosphates of these islands consist chiefly of aluminium

phosphate. They are quite unsuitable for the manufacture of superphosphate. They have been dissolved in sulphuric acid, and the alumina separated as alum. It has also been found possible to obtain a large proportion of the phosphoric acid as sodium phosphate by heating with sodium chloride in superheated steam, or by firing with sodium sulphate and carbon (J. Soc. Chem. Ind. 1886, 570).

Bordeaux phosphate. Raised in the departments of Lot and Tarn-et-Garonne. This is now little used in England, as it is not rich in phosphate, and contains a good deal of ferric oxide and alumina.

Nassau or Lahn phosphate. This is still used locally, but the exports to this country have ceased. It varies much in composition; the higher qualities are suitable for the manufacture of superphosphate, but the lower qualities contain much iron. This phosphate is remarkable as containing a distinct amount of iodine.

Coprolites. The phosphatic nodules commonly known as coprolites, found in England, are scarcely used now, cheaper phosphates being available. The Cambridge (Upper Greensand) coprolite was the best of the English sorts; it contained 55–60 p.c. tricalcium phosphate, without an admixture of ingredients prejudicial to the production of soluble phosphate. The Suffolk coprolite (Tertiary) contains less phosphate (55 p.c.), and more ferric oxide. The Bedfordshire coprolite (Lower Greensand) is still more inferior, the ferric oxide being present in increased proportion.

In France there are considerable deposits of coprolite in the Upper Greensand in the departments of Pas de Calais, Meuse, and Ardennes; those from Pas de Calais are shipped to England from Boulogne. These coprolites generally contain a low proportion of phosphate, and much silicious matter.

Deposits of coprolite have also been found in Russia.

Florida phosphate. Extensive deposits of high-grade phosphate have been opened up during recent years in the State of Florida. The phosphate is of two kinds, namely, 'hard rock' phosphate and 'pebble' phosphate. The rock phosphate commonly contains from 78 to 80 p.c. of tricalcium phosphate, and the pebble phosphate about 70–74 p.c. There is, however, also a high-grade pebble phosphate, found in the Medulla and Coronet mines, containing from 78 to 79 p.c. of tricalcium phosphate. These phosphates are very widely used in superphosphate. According to the estimates of Voss, 600,000 tons of Florida 'hard rock' phosphate and 900,000 tons of Florida 'pebble' phosphate were raised during 1908.

African phosphate. An extensive range of phosphate deposits is now worked on or near the northern coast of Africa, and is known in commerce as Algerian, Tunisian, Tocqueville, and Gafsa phosphates. These are soft, powdery, or friable minerals, containing for the most part comparatively little silicious matter, but a large proportion of calcium carbonate. The proportion of tricalcium phosphate is commonly somewhere near 60 p.c., varying from about 59 p.c. to nearly 64 p.c. The quantities of North African phosphate mined in 1908 were estimated by Voss at over 1,500,000 tons. Algerian phosphate has the special advantage of containing a very low proportion of alumina and ferric oxide.

Christmas Island phosphate. This is a deposit found on Christmas Island—an island lying in the Indian Ocean south of Java. It contains about 87 p.c. of tricalcium phosphate, and makes excellent superphosphate. At present the output is said to be largely consumed in the manufacture of superphosphate in Japan.

Pacific phosphate. Valuable deposits of similar high-grade phosphates, containing 86 or 87 p.c. of tricalcium phosphate, accompanied by very little ferric oxide or alumina and practically no silica, have been discovered in recent years on certain islands in the Pacific Ocean lying to the north-east of Australia. The principal deposits at present worked are those of Ocean Island and Nauru Island, but deposits have also been found on the islands of Makatea, Tahiti, and Angaur. Much of the phosphate raised on these islands is consumed for superphosphate making in Australia, New Zealand, and Japan. The total quantity raised in 1908 from these various islands (including Christmas Island) was estimated by Voss at 350,000 tons.

PERCENTAGE COMPOSITION OF MINERAL PHOSPHATES EMPLOYED IN THE MANUFACTURE OF SUPERPHOSPHATE.

FLORIDA PHOSPHATES. (Dried at 100°.)

—	Hard rock			Pebble, medium grade				Pebble, high grade	
*Phosphoric acid (P_2O_5)	36·05	36·44	36·81	31·92	32·24	32·80	33·98	36·24	35·90
Lime	51·29	50·46	50·96	46·76	46·78	47·18	48·03	49·44	48·68
Alumina	1·42	1·44	1·41	1·28	1·29	1·32	1·23	1·32	
Ferric oxide (exclusive of any pyrites)	0·60	0·60	0·55	1·45	1·50	1·85	1·05	0·60	9·20
Magnesia, carbonic acid, fluorine, &c.	7·84	6·31	6·67	11·66	10·43	9·50	9·46	6·40	
Silicious matter	2·80	4·75	3·60	6·93	7·76	7·35	6·25	6·00	6·22
	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00
*Equal to tricalcium phosphate	78·77	79·62	80·43	69·75	70·44	71·67	74·25	79·18	78·44
Excess of lime over tricalcium phosphate	8·57	7·28	7·34	8·93	8·58	8·31	7·76	6·50	6·14
Moisture in phosphate as imported	0·66	1·60	—	2·11	1·94	2·03	2·33	—	—

NORTH AFRICAN PHOSPHATES.
(Dried at 100°.)

—	Algerian		Tocqueville	Tunisian		Gafsa
*Phosphoric acid (P_2O_5)	27·05	29·04	25·26	27·21	28·44	27·12
Lime	47·79	50·46	43·01	48·83	49·92	44·87
Alumina	0·56	0·44	0·52	0·54	0·48	0·96
Ferric oxide (exclusive of any pyrites)	0·25	0·30	0·48	0·30	0·25	0·40
Magnesia, carbonic acid, fluorine, &c.	18·95	16·96	17·33	17·66	17·41	18·95
Silicious matter	5·40	2·80	13·40	5·46	3·50	7·70
	100·00	100·00	100·00	100·00	100·00	100·00
*Equal to tricalcium phosphate	59·10	63·45	55·19	59·45	62·14	59·26
Excess of lime over tricalcium phosphate	15·74	16·05	13·08	16·59	16·22	12·73
Moisture in phosphate as imported	—	—	—	3·30	3·24	—

VARIOUS PHOSPHATES.
(Dried at 100°.)

—	Christmas Island	Ocean-Nauru	Tennessee	Belgian	French	Canadian	
						Rich	Poor
*Phosphoric acid (P_2O_5)	39·85	39·84	36·92	19·57	23·80	39·32	29·99
Lime	52·24	53·05	50·59	49·34	52·96	54·18	42·25
Alumina	1·35	0·30	1·59	0·43	1·44	0·40	2·84
Ferric oxide (exclusive of any pyrites)	0·45	0·23	1·70	0·65	0·60	0·55	2·03
Magnesia, carbonic acid, fluorine, &c.	5·96	6·48	7·46	26·23	20·60	4·11	9·27
Silicious matter	0·15	0·10	1·74	3·78	0·60	1·44	13·62
	100·00	100·00	100·00	100·00	100·00	100·00	100·00
*Equal to tricalcium phosphate	87·07	87·05	80·60	42·76	52·00	85·84	65·47
Excess of lime over tricalcium phosphate	5·02	5·84	6·91	26·15	24·76	7·66	6·77
Moisture in phosphate as imported	1·54	2·52	1·21	0·45	—	—	4·86

—	Spanish		West Indian		Coprolites		South Carolina
	High grade	Poor	Aruba	Curaçao	Bedfordshire	Suffolk	
*Phosphoric acid (P_2O_5)	35·01	25·77	33·63	32·73	25·97	26·30	26·73
Lime	48·49	34·58	48·33	47·29	40·66	41·72	43·62
Alumina	1·79		1·63	0·35	1·48		0·83
Ferric oxide (exclusive of any pyrites)	1·05	7·10	1·75	0·75	5·30	22·90	1·45
Magnesia, carbonic acid, fluorine, &c.	7·98		12·10	18·38	14·03		17·77
Silicious matter	5·68	32·55	2·56	0·50	12·56	9·08	9·60
	100·00	100·00	100·00	100·00	100·00	100·00	100·00
*Equal to tricalcium phosphate	76·43	56·26	73·48	71·45	56·69	57·42	58·35
Excess of lime over tricalcium phosphate	7·07	4·09	8·48	8·57	9·94	10·60	12·00
Moisture in phosphate as imported	—	1·17	3·04	—	0·65	1·41	0·90

Manufacture of superphosphate. The raw phosphate is first reduced to an extremely fine powder. Considerable improvements have now been effected both in the economy of the grinding and in the degree of fineness attained. If the material is in large lumps, it is first reduced by means of a crusher, and is then transferred to a suitable mill. The Kent mill is largely used for this purpose, and is worked in conjunction with a screen and elevator. The finer the powder obtained, the more complete will be the decomposition by the sulphuric acid. For first-class work the powder should pass through a sieve of 80 wires to the inch. In view of the stringency of modern factory legislation, a dust-collecting plant of some sort, such as the Beth filter, is usually considered necessary in the part of the works devoted to milling.

It has been assumed in some text-books that the reaction in superphosphate making is simply:

$$Ca_3P_2O_8+2H_2SO_4=CaH_4P_2O_8+2CaSO_4.$$

This is true as regards the major portion of the phosphate rendered soluble. But in practice, as was first pointed out by Ruffle (J. Soc. Chem. Ind. 1887, 327), the reaction, as regards an appreciable portion of the phosphate, almost invariably proceeds further, thus:

$$Ca_3P_2O_8+3H_2SO_4=2H_3PO_4+3CaSO_4,$$

so that a water solution of superphosphate contains a major proportion of $CaH_4P_2O_8$, with a minor proportion of free phosphoric acid H_3PO_4. Indeed, unless there is a fair proportion of the latter, the proportion of 'soluble' phosphate is unstable, owing to liability to reversion by subsequent interaction between the dissolved phosphate and that which was originally left undissolved. Thus well-made superphosphate, when freshly made, often contains as much as from 6 to 10 p.c. of H_3PO_4, and sometimes more.

In the first stage of the reaction, phosphoric acid alone is probably produced, and this afterwards reacts on the remaining undecomposed phosphate. The proportion of free phosphoric acid in the resulting manure is greater when strong sulphuric acid has been employed, the total soluble phosphoric acid being, at the same time, diminished. When superphosphates are dried at 100°, a loss of soluble phosphoric acid also occurs, and this loss becomes much greater when a higher temperature is employed (Ruffle). Monocalcium phosphate can, in fact, exist only when in union with water.

A further reaction which is of great practical moment to the manufacturer of superphosphate is the disappearance of soluble phosphate by keeping. The regenerated insoluble phosphate is known as 'reverted phosphate.' This deterioration during storage is not observed in the case of well-made superphosphate prepared from finely ground mineral phosphate containing no appreciable quantity of iron or aluminium, but it is observed when ferric oxide or alumina is present.

So long as superphosphate is valued on the basis of its contents in soluble phosphate, ferruginous and aluminous phosphates will be avoided by the manufacturer. On the Continent, however, and in the United States, reverted phosphate has a considerable money value, and mineral phosphates containing iron and aluminium consequently find employment.

The sulphuric acid employed is usually pyrites-made chamber acid of 1·55 to 1·60 sp.gr. Weak acid is essential, as the dryness of the superphosphate depends largely upon sufficient water being present for the crystallisation of the calcium sulphate ($CaSO_4,2H_2O$) formed by the reaction. It follows that, when much calcium carbonate is present in the phosphate, weaker acid will be required than when but little calcium carbonate is present. When calcium fluoride is present in considerable quantity, and very little or no calcium carbonate (as in apatite), acid stronger even than 1·60 sp.gr. is necessary, as calcium fluoride is not so readily decomposed as calcium carbonate.

The proportion of sulphuric acid to be used depends, of course, upon the composition of the phosphatic material. Theoretically, 100 of tricalcium phosphate will require 94 of sulphuric acid of sp.gr. 1·60 (55 p.c. SO_3), or 100 of sulphuric acid of sp.gr. 1·55 (51·5 p.c. SO_3), if monocalcium phosphate is to be produced. The proportion of sulphuric acid used in practice is usually as large as can be employed without endangering the dryness of the product. It is generally somewhat in excess of that needed to produce monocalcium phosphate, but is considerably below that required to yield only phosphoric acid. For South Carolina river phosphate, the ordinary proportion is 95 p.c. of sulphuric acid of sp.gr. 1·57.

The excess of lime present in the material (as carbonate or fluoride) is a principal factor in determining the quantity of sulphuric acid to be employed: 100 of lime will require 260 of acid sp.gr. 1·6 or 277 of acid sp.gr. 1·55 to produce calcium sulphate. At the foot of the table previously given will be found the excess of lime (over that required to form tricalcium phosphate) present in each of the mineral phosphates commonly employed. Phosphates containing a considerable excess of lime will yield a poorer superphosphate than their percentage of phosphoric acid would seem to warrant, owing to the large proportion of sulphuric acid which they require.

To prepare a 'mineral superphosphate,' the only ingredients are the powdered phosphate and sulphuric acid. When turnip manures, or other manures containing a little nitrogen, are prepared, crushed bones, powdered hoof and horn, shoddy, or ammonium salts, are added when the ingredients are mixed. Mixed superphosphates, formerly called 'dissolved bones,' are usually prepared from a mixture of mineral phosphate, bone, and some concentrated nitrogenous matter.

Owing to the requirements of the Fertilisers and Feeding Stuffs Act, however, such mixtures are now sold as 'dissolved bone compounds,' the term 'dissolved bone' or 'vitriolised bone' being restricted to fertilisers made from pure bone and acid only. Usually, in such cases, only from one-half to two-thirds of the phosphate is actually soluble in water, but much of the remainder is in the readily assimilable form of dicalcium dihydrogen phosphate. If enough acid were used to dissolve all the phosphate, the product would be too pasty for sowing.

The mixer in which the reaction takes place

stands on a platform, over an empty chamber, variously known as the 'bin,' 'den,' or 'pit.' It consists of a cylinder, sometimes nearly horizontal, sometimes vertical, furnished in the centre with a revolving shaft, carrying arms set on screw-wise. Into this mixer the charge of weighed 'dust' is emptied, bag by bag, while, at the same time, a measured quantity of sulphuric acid is run in from a tank. When the charge is completed, agitation is continued for two minutes; a valve is then opened, and the whole contents of the mixer (about 16 cwt.) allowed to fall into the pit below. Ten charges can be easily worked in one hour. The pit below is built of brick or concrete on three sides, the fourth side consists of a wooden hoarding which is taken down when the pit is being emptied. A pit will hold from 80 to 140 tons. The fluid material which enters the pit rapidly reaches a temperature considerably exceeding 100°, and then becomes solid. In a few hours it is ready to be excavated.

Until recently, the excavation of the superphosphate had always been accomplished by the simple means of digging it out by the aid of pickaxes. At the present time, however, manual labour is being gradually superseded by the use of mechanical appliances, many patents for inventions for doing this part of the work having been taken out. Among these, one of the best known is the superphosphate excavator of Dr. A. Keller, of the Anglo-Continental Guano Works of London, Hamburg, Antwerp, and Düsseldorf, which is now in successful use in various parts of the world. This machine consists of an arm extending from a staging, which latter travels upon metals laid in front of the pit; the arm is furnished with travelling knives and scrapers, and it revolves on a pivot around the staging as a centre, so that it can be swung in and out of the pit and be made to reach to the extreme back part of it. When the knives and scrapers are set in motion, the superphosphate is scraped forward and dropped on to a conveyor traversing the front of the pit, whence it can be elevated and conveyed to the part of the works where it is required to be stored. The machine is so constructed that the arm is made to move from left to right and *vice versâ*, and lower itself automatically as the superphosphate is removed.

The gases given off during the reaction, both from the mixer and pit, are of a particularly unpleasant description, especially when the phosphate contains fluorides. Both mixer and pit are provided with flues in connection with a fan, by which all the gases are removed; these are purified in a scrubber, and then conducted to a tall chimney.

Well-made superphosphate is a porous mass, the cavities being due to imprisoned gas. It is usual to break up the lumps at the time of manufacture by passing it through a rotary screen, and to further grind and screen it after storing and before delivery. If mixed manures are to be made, the other ingredients are added while passing through the disintegrator.

By adding ammonium sulphate or other nitrogenous material, with or without potash salts, 'corn,' 'grass,' 'mangel,' and 'potato' manures are produced. Sodium nitrate cannot safely be added to superphosphate unless the latter is very dry; if this precaution is neglected, free nitric acid is produced, the manure bags are destroyed, and serious mischief may occur. To employ ammonium sulphate and sodium nitrate together is still more objectionable, as ammonium nitrate is formed, and even when it does not suffer decomposition it ruins the manure by its deliquescence.

Ordinary superphosphate is made from a mixture of phosphates, and contains 26 p.c. of dissolved phosphate (=11·9 p.c. P_2O_5) and 2–3 p.c. of undissolved phosphate. The turnip manures containing bone have generally rather less of dissolved phosphate, more of undissolved, and nearly 1 p.c. of nitrogen. Special manures of greater strength are also prepared. From high-class phosphate, superphosphate containing 30–31 p.c. dissolved phosphate (13·7–14·2 P_2O_5) may be obtained. High-grade Florida rock will yield superphosphate containing 38–39 p.c. dissolved phosphate (17·4–17·9 P_2O_5). From Ocean Island and Christmas Island phosphates, superphosphate with 44–45 p.c. dissolved phosphate (20·2–20·6 P_2O_5) may be prepared.

Far richer superphosphates are obtained by the process patented by Packard (Eng. Pat. 6176, 6750, 6752). Superphosphate, prepared so as to be rich in free phosphoric acid, is extracted with water, the solution evaporated to sp.gr. 1·125–1·300, and sufficient calcium phosphate, carbonate, or hydroxide added to leave one-third of the phosphoric acid in the free state. The solution is then filtered, and the filtrate evaporated to dryness. The product contains about 40 p.c. of soluble phosphoric acid, equal to 87 p.c. of so-called 'soluble phosphate.' This superphosphate has a special value where manure has to be conveyed a long distance.

There is a large export trade in English-made superphosphate.

Gypsum. This has in most cases a very small value as a manure. Where superphosphate is employed, it is applied in this manure. Massive gypsum is imported from the South of France. It was formerly used as a diluent in making the lower class of superphosphates, but its place is now taken by Belgian phosphate. It is an excellent drier for mixing with damp manure.

Lime, chalk, and marl. These can hardly be classed as artificial manures, as they are not generally applied as plant foods, but for the sake of the considerable amelioration of the soil which they effect.

Potassium salts. These will be found described under their own head.

The Relative Value of Manures.

We have described as briefly as possible the various nitrogenous and phosphatic manures at present used. The important question remains, Have the nitrogen and phosphoric acid the same value in all these manures? and, if not, what is the difference of value? This question may be considered from (1) a trade point of view, viz. by calculating from the market price of various manures what is the money value of their chief constituents. If the prices given for manures were determined by an accurate knowledge of their effect in the field, these prices would really show us their average relative value. As a fact, market prices do generally indicate,

though sometimes very imperfectly, the relative manuring value of different manures. The matter may also be considered from (2) the data afforded by actual investigation. In this case, we soon find that the number of available investigations is insufficient, and that the relative value of the same manures differs more or less with differences in the soil, crop, and season. Certain points, however, are fairly well established.

Nitrates are, in a large majority of cases, the most active, and therefore the most valuable, form of nitrogen. Comparisons between sodium nitrate and ammonium salts, containing similar amounts of nitrogen, have been made for many years at Rothamsted, and also at Woburn. With cereal crops the nitrate, on an average, yields distinctly more corn and considerably more straw than the ammonia. The produce by the nitrate is most in excess in dry seasons; in a wet season the ammonia may be superior. On pasture, the relative superiority of the nitrate is about the same as with cereals. With potatoes, ammonia, apparently, is equal to nitrate. With mangel-wurzel, or sugar beet, the nitrate is far superior. A good result with ammonium salts is much more dependent on the presence of abundance of phosphates and potash in the soil than is the case with nitrates. Nitrates and ammonium salts, in favourable circumstances, give all their effect in the first year of their application.

Cyanamide, under favourable conditions, gives results similar to those obtained from a corresponding quantity of ammonium sulphate, but its action depends upon its time of application and upon suitable weather, and probably upon the texture and composition of the soil, as well as on biological considerations. It is best used after admixture with superphosphate, though it has the incidental effect of 'precipitating' soluble phosphate. It is not a pleasant substance to handle in its raw condition, and, if sown alone, it should be sown by means of a mechanical distributor.

The effect of organic nitrogenous manures differs in different soils. In a clay soil, bones decompose so slowly as to be of little value. Organic manures, as shoddy, oilcake, bones, and farmyard manure, yield only a small portion of their nitrogen to the crop during the first year, and several years will elapse before the supply is exhausted. The continued use of such manures increases the proportion of nitrogen in the soil. The proportion of the nitrogen in the manure that is recovered in the crop is frequently smaller than that obtained under favourable circumstances in one season from the application of sodium nitrate, the slowly acting manures being, in the case of arable land, subject to an annual loss of nitrogen as nitrates by drainage. Organic nitrogenous manures are more active in proportion as they are finely divided, and when applied to a well-aërated soil. They are best applied in autumn, while nitrates and ammonium salts should be applied in spring.

Pot culture experiments have been made by Wagner on various nitrogenous manures. If the crop yield obtained from sodium nitrate be represented by 100, the relative efficacy of a like quantity of nitrogen supplied in other fertilisers proved to be as follows:—

Sodium nitrate	100
Ammonium salts	94
Peruvian guano	87
Green plants	77
Horn meal	74
Dried blood	73
Castor cake	73
Wool-dust	26
Cow manure	22
Leather meal	16

But it does not necessarily follow that these figures represent the relative value of the fertiliser in all the varied conditions of practical farming. This subject is being investigated by field trials at Rothamsted.

The relative value of different forms of phosphates has been a subject of much controversy. Some mineral phosphates (as apatite) having been found almost useless as manure, it was too hastily concluded that (with the exception of bone and guano phosphates), only phosphates soluble in water were effective. It has been maintained that very fine grinding will render any phosphate as available as soluble phosphate.

In considering the subject we should bear in mind that the phosphates in the soil, on which plants feed, are not soluble in water, drainage waters being free from phosphoric acid. Soluble phosphate when applied to a fertile soil is quickly precipitated, and is generally finally converted into a hydrated ferric or aluminium phosphate. The practically insoluble phosphates of the soil are dissolved by the acid sap of the root hairs immediately before absorption by a crop or by the carbonic-acid-laden water of the soil.

One great advantage possessed by a phosphate soluble in water consists in its diffusibility. When rain falls after an application of superphosphate, the phosphoric acid is distributed in the soil more perfectly than can be achieved by any other mode of application, and consequently a greater number of root hairs may come in contact with it. Superphosphate is thus more immediately effective than any other form of phosphate. The superiority of superphosphate is, however, not shown in the case of some soils very poor in lime, and in which any additional supply of acid matter is hurtful to the plant; in such cases an assimilable undissolved phosphate may produce a better result.

In view of this, an article known as 'basic superphosphate' is, on the suggestion of Mr. John Hughes, sent out by various manufacturers. It consists of superphosphate neutralised by admixture with sufficient lime to convert the originally soluble phosphate into 'precipitated' or 'reverted' phosphate.

On such soils (poor in lime), basic slag, Peruvian guano, or fine bone meal, also find an appropriate place.

Numerous experiments have been made regarding the assimilability of mineral phosphates when finely ground. It appears that apatites and other crystalline phosphates not disintegrated in the soil, have a very small effect as manure even when finely ground. The small crystalline grains of the Somme phosphate lie in this category. The majority of mineral phosphates are, however, effective as manure when very finely ground, but to a different extent on different soils. The conditions favourable to the use of undissolved phosphates are

presence of humus and absence of lime. On the moor soils of Germany, where such conditions prevail, basic slag has had its greatest success. A calcareous soil is the one most unsuitable for the use of undissolved phosphates, calcium carbonate offering a great resistance to the solution of calcium phosphate (Chem. Soc. Trans. 1866, 313).

It is generally admitted that precipitated dicalcium phosphate is nearly equal in effect to soluble phosphate. Phosphates that are soluble in ammonium citrate (including the reverted phosphate of superphosphate) may be safely regarded as assimilable by plants; in America they are regarded as of about equal value with water-soluble phosphate; that they are so always is certainly open to doubt. Phosphates that are insoluble in ammonium citrate are often effective as manure. Ammonium citrate gives thus no safe distinction between assimilable and non-assimilable phosphates, though it affords a useful approximate means of determining 'reverted' phosphate in superphosphate.

As a measure of ready availability in basic slag, a 2 p.c. solution of citric acid has now superseded ammonium citrate.

Special Methods of Analysis.

The enormous quantity of artificial manures bought and sold upon the results of analysis has led to great attention being paid to the question of accurate and speedy analytical methods. To enter into a discussion of all the methods which have been suggested, or even of those which have been 'officially' recognised by the associations of agricultural analysts in different countries, is here impossible.

In the analysis of fertilisers, the object is sometimes merely the determination of a definite fact, such as the percentage of total nitrogen or the percentage of total phosphoric acid. In such cases there are divers processes serving to arrive at the same results. Sometimes, however, the analysis is needed for such a purpose as the determinations of 'soluble' phosphate. Here much depends upon the interpretation of the word 'soluble,' since solubility depends not merely on the nature of the solvent, but upon its proportion to the material acted upon and the mode and duration of its application. It is therefore necessary to define 'solubility' before determining it. Unfortunately, different interpretations of solubility have been in vogue in different countries, causing occasional confusion in international trade, but recent efforts to arrive at international agreement have been attended with some measure of success.

Analysis of Raw Mineral Phosphates.

Determination of phosphoric acid. The phosphoric acid in mineral phosphates may be accurately determined either by the use of molybdic acid or by what is sometimes called the citric-oxalic-magnesium process, without the intervention of molybdic acid.

There are several modifications of the molybdate process which give fairly accurate and therefore concordant results in the hands of careful workers. Their one common disadvantage is that the quantity of sample represented in the portion of solution finally worked upon is necessarily smaller than in the alternative procedure, and consequently any errors due to inaccuracy of calibration of flasks or pipettes or to lack of exactness in using them, are correspondingly multiplied; and the same observation obviously attaches to errors incidental to the washing of precipitates, the efficiency of filters, and the operations of weighing. There is cogent reason for supposing that many disagreements sometimes attributed to the use of alternative processes are due to insufficient appreciation of some of these sources of error, or to the non-observance of the precautions necessary to avoid them. Considerations of the pecuniary cost of molybdic acid sometimes afford a temptation to operate on far too small a scale, and this temptation should be resisted. Thus, many continental analysts were for years content to operate on as little as 0·2 gram of raw phosphate. In such a case, a single milligram of magnesium pyrophosphate (the form in which the phosphate is weighed) is equivalent to approximately 0·7 p.c. of tricalcium phosphate—a grave consideration in the case of large cargoes, the price of which is exactly adjusted to the results of analysis, even to the second place of decimals.

Two modifications of the molybdic process as applied to the analysis of raw mineral phosphates may be given, the first being that of G. Jörgensen, who has devoted much time and attention to the matter, the other that communicated by Dr. M. Ullmann, on behalf of the Verein Deutscher Dunger-Fabrikanten, to the International Congress of Applied Chemistry in London in 1909. Jörgensen's process was originally published in Denmark, but an account of it, communicated by himself, is published in the Analyst, 1909, 34, 392. As there are some differences of detail between the processes, both of which yield accurate results, they may be given side by side. It will be seen that Jörgensen operates finally on a quantity corresponding to 1 gram of the original material, whilst in Ullmann's process the quantity is halved. 1 gram can, however, be equally well taken by doubling the quantity of reagents.

Reagents used.

Solvent.

Jörgensen.	Ullmann.
Nitric acid of sp.gr. 1·21.	*Aqua regia* (3 parts hydrochloric acid of sp.gr. 1·12, and 1 part nitric acid of sp.gr. 1·2).

Molybdic Solution.

100 grams of ammonium molybdate are dissolved in 280 c.c. of ammonia of sp.gr. 0·97, and 300 c.c. of this solution poured with vigorous shaking into 700 c.c. of nitric acid of sp.gr. 1·21, the mixture being allowed to stand for 24 hours.	150 grams of ammonium molybdate are dissolved in 500 c.c. of water. This solution and a separate solution of 400 grams of ammonium nitrate are mixed and made up to 1 litre. The mixture is poured into 1 litre of nitric acid of sp.gr. 1·2, and allowed to stand for 12 hours at 60°, or for 24 hours at the ordinary temperature.

Wash Fluid for Molybdic Precipitate.

40 grams of ammonium nitrate and 10 grams of nitric acid per litre. The author prepares this by mixing 90 c.c. of nitric acid of sp.gr. 1·4 with about 1500 c.c. of water, adding 80 c.c. of ammonia of sp.gr. 0·91 and making up to 2 litres.	32 grams of nitric acid of sp.gr. 1·2 and 50 grams of ammonium nitrate, made up to 1 litre.

Magnesia Mixture.

50 grams of pure crystallised magnesium chloride and 150 grams of pure ammonium chloride, dissolved and made up to 1 litre.	50 grams of pure crystallised magnesium chloride and 150 grams of pure ammonium chloride, dissolved and made up to 1 litre.

Wash Fluid for Ammonium-Magnesium Precipitate.

Ammonia solution containing 2½ p.c. NH_3. (This may be made by diluting 100 parts of ammonia of sp.gr. 0·91 with water to 1 litre.)	Ammonia solution containing 2½ p.c. NH_3.

Method of Jörgensen. Five grams of the mineral phosphate are dissolved in 20 c.c. of nitric acid in a 250 c.c. flask. After gentle boiling for 15 minutes, the contents of the flask are cooled, made up to 250 c.c., and filtered. To 50 c.c. of the filtrate (=1 gram of the phosphate) in a beaker-flask, 165 c.c. of the molybdic solution are added, and the flask and its contents placed in a water-bath at a temperature of 50° for 10 minutes, with occasional stirring. After cooling and standing, the supernatant liquid is poured through a filter and the precipitate is washed 10 times by decantation with the acid ammonium nitrate solution, about 20 c.c. being used for each washing. The filtrate should be tested with more molybdic solution to see that the precipitation is complete. The washed precipitate is dissolved in 100 c.c. of 2½ p.c. ammonia solution, and filtered, if necessary, through the filter which served for its separation, the filter being washed 8 times with ammonia solution, until the final volume is about 180 c.c. The beaker-flask is covered with a clock-glass, the contents brought just to boiling-point, and 30 to 35 c.c. of the magnesia mixture added drop by drop from a burette, the whole being well stirred and allowed to cool with frequent stirring as long as it remains. If the precipitate is not compact and crystalline, the stirring during this time should be continuous. After standing for at least 4 hours, the precipitate is filtered off, using a platinum (Gooch) crucible packed with spongy platinum, and washed with the 2½ p.c. ammonia solution until free from chlorides, and once with alcohol. It is then dried, heated (at first gently), and then ignited strongly, cooled, and weighed as $Mg_2P_2O_7$.

Method of Ullmann. To 5 grams of the phosphate in a 500 c.c. flask, 50 c.c. of *aqua regia* are added, the whole being evaporated nearly to the consistency of syrup for the elimination of silica. The residue, after setting to an approximately solid mass, is taken up with 10 c.c. of nitric acid (of sp.gr. 1·2) and 50 c.c. of water, boiled, cooled, made up to 500 c.c. with water, and filtered. 50 c.c. of the filtrate (=0·5 gram of the phosphate) are treated with an excess of molybdic solution (at least 100 c.c. for every 0·1 gram of P_2O_5), and digested in a water-bath at 50° for 1 hour. After sufficient standing, the supernatant liquid is poured through a small close filter, and the precipitate washed repeatedly by decantation until free from calcium. At least five washings with 20 c.c. each time are recommended. The filtrate should be tested with molybdic solution to see that the precipitation has been complete. The precipitate is dissolved with from 80 to 100 c.c. of the 2½ p.c. ammonia solution, and filtered through the same filter which served for its separation. The filter should then be washed five or six times with hot water, until the total volume of the solution is from 130 to 150 c.c. The solution is warmed to 60° or 80°, and immediately precipitated with 20 c.c. (or a sufficiency) of the neutral magnesia mixture, added drop by drop with constant stirring. After at least 4 hours' standing, followed by half an hour's stirring, the precipitate is allowed to rest, filtered, and washed with 2½ p.c. ammonia solution until the washings are free from chlorine. The precipitate is dried, gently heated, ignited to constancy, and weighed as $Mg_2P_2O_7$.

CITRIC-OXALIC-MAGNESIUM PROCESS.

The phosphoric acid (and incidentally the lime) may be correctly determined in the following way. Two grams of the mineral phosphate are treated with 25 c.c. of strong hydrochloric acid in a beaker covered with a clock-glass to avoid loss by spraying. After a few minutes' warming, the clock-glass is washed back into the beaker and removed, the beaker being placed in a water-bath and the contents evaporated to dryness. This results in the elimination from solution of not only silica, but of fluorine compounds, the removal of which is essential to the accuracy of the process. Mere evaporation to dryness with a small quantity of hydrochloric acid is insufficient to ensure this removal. It is necessary to use at least the large quantity of acid specified (25 c.c.), so that its evaporation may extend over several hours. (The non-observance of this precaution is a fruitful source of error, resulting in the subsequent formation of magnesium fluosilicate and consequent over-estimation of phosphoric acid.) The dry residue is taken up with 5 or 10 c.c. of hydrochloric acid and about 20 c.c. of water, and warmed. The silica, together with pyrites or other insoluble matters, is filtered off and thoroughly washed. To the filtrate and washings (measuring about 150 c.c.), 4 grams of powdered citric acid are added and 3 to 4 grams of powdered ammonium oxalate. The solution is heated nearly to boiling, and rendered just alkaline with dilute ammonia (sp.gr. about 0·970) and excess of acetic acid is immediately added and the liquid is boiled for a few moments. The calcium oxalate is immediately filtered off and washed several times with boiling water, dried, and ignited over a yellow argand flame,

and weighed as $CaCO_3$. The precipitate contains all the calcium. It may contain very minute quantities of ferric oxide, aluminium oxide, or manganese oxide, and a minute quantity of phosphoric acid. On this account the precipitate, after being weighed, is dissolved in dilute hydrochloric acid, the solution being boiled and treated with a slight excess of recently diluted ammonia. The small precipitate which forms is filtered through a small filter, washed, and redissolved in a little dilute acid, the solution being boiled and again treated with a slight excess of ammonia. The precipitate is washed, ignited, and weighed. If this small precipitate weighs only 5 or 6 milligrams or less (as is usually the case in the hands of a practised worker), it may be assumed that the precipitate contains P_2O_5 equal to half its own weight of $Mg_2P_2O_7$, this assumption being based on the analysis of a large number of such precipitates. But if, owing to unskilful work or to any peculiarity in the mineral under investigation, the quantity is greater, the little precipitate may be redissolved in hydrochloric acid, with the addition of about 0·1 gram of citric acid, and its solution added to the original filtrate from the calcium oxalate precipitate.

This filtrate is made strongly ammoniacal and the phosphoric acid precipitated by the gradual addition of magnesium mixture, a large excess being finally added. The gradual addition and vigorous stirring are both necessary to ensure that the precipitate comes down in a compact crystalline form. The whole bulk at this stage will be about 350 c.c. After 2 to 3 hours, during which the liquid is frequently stirred—or after standing, if more convenient, over-night—the greater part of the liquid is decanted off through a close filter, leaving about 40 c.c. of it in the beaker with the precipitate. The filter is washed with dilute hydrochloric acid, the washings being used to redissolve the precipitate in the beaker. After complete re-solution, the contents of the beaker are rendered ammoniacal by slowly dropping in dilute ammonia with vigorous stirring until the precipitate assumes as before a dense crystalline form. Excess of ammonia solution (sp.gr. 0·880), equal to about one-fifth or one-sixth of the bulk of the liquid, is added and the whole allowed to stand with occasional vigorous stirring for at least one hour. The precipitate is then filtered, washed well with ammonia (sp.gr. 0·970), dried, ignited, and weighed as $Mg_2P_2O_7$.

The re-solution and second precipitation of the ammonium magnesium phosphate is an essential feature of the process, since in the first precipitation small quantities of magnesium oxalate are usually formed. The non-observance of this precaution has been a frequent source of 'high' results.

The presence of ammonium citrate and ammonium oxalate results in the retention in solution of a minute quantity of P_2O_5. In earlier days it was usual to precipitate the ammonium magnesium phosphate, in a flocculent form, by the sudden addition of ammonia and magnesium mixture, and under these circumstances (*see*, for example, the original directions of Fresenius) a very substantial correction was necessary for solubility of the precipitate. Crystalline precipitation, however, reduces this to a minimum, and the accurate determination by molybdic acid of the phosphoric acid in the evaporated and ignited filtrates obtained in a large number of analyses of numerous grades and varieties of phosphate indicates that, if the process be carried out as here described, the quantity of P_2O_5 which escapes precipitation corresponds to an average of approximately 0·0025 gram of $Mg_2P_2O_7$, which quantity must be added to the weight of $Mg_2P_2O_7$ obtained, together with half the weight of the small ammonia precipitate (obtained from the calcium oxalate precipitate), unless this was redissolved into the main filtrate (*see* above).

If the precautions herein set forth are observed, the results will be identical with those obtainable by the accurate working of the molybdic process as defined by Jörgensen or by Ullmann.

Direct Magnesium Precipitation without Removal of Calcium.

This process consists in adding to the acid solution of the phosphate a large excess of citric acid, sufficient to prevent calcium precipitation, and of ammonia, and in the direct precipitation of the phosphoric acid by magnesium mixture, without re-solution. This process (with certain precautions) answers well for basic slag (*see* later), and in some hands appears to give good results with mineral phosphates. It does not, however, answer equally well for all phosphates, and the result, even when accurate, owes its success to a balance of positive and negative errors, since the precipitate finally weighed does not consist of pure $Mg_2P_2O_7$, as is assumed to be the case. For rough work, as in phosphate prospecting, when an error of 0·5 p.c. or so is of no moment, it is excellent, being expeditious and involving a minimum of trouble. It is essential that silica should be eliminated by preliminary evaporation of the acid solution to dryness as in the preceding section.

Determination of Ferric Oxide and Alumina in Mineral Phosphates.

The solvent used should be hydrochloric acid rather than *aqua regia*. The latter is sometimes recommended. For many phosphates it is perhaps immaterial which solvent is used. But some phosphates (such as American river pebble phosphates) contain much pyrites. If *aqua regia* is used, this is dissolved and included as ferric oxide—which is misleading, seeing that pyrites is not attacked by the sulphuric acid used in superphosphate making, and is consequently non-injurious. It should, therefore, be eliminated with the silica, as is the case if hydrochloric acid be used as the solvent.

There are two methods in use which accurately determine ferric oxide and alumina.

Acetate Method.

Two grams of phosphate are treated with strong hydrochloric acid. The solution is evaporated to dryness and the residue redissolved in acid and water and filtered from the silicious residue. The filtrate is oxidised by addition of bromine water until orange coloured, nearly neutralised with ammonia, cooled and precipitated with a good excess of ammonium acetate solution containing an excess of acetic

acid. After standing some hours, the precipitate is filtered off and washed with hot water.

The bulky precipitate contains all the ferric oxide and alumina (as phosphates), together with a varying quantity of calcium phosphate. It is dried, ignited, and weighed. It is then dissolved in a very small quantity of hydrochloric acid and about 1 gram of citric acid and 0·5 gram of ammonium oxalate added, slight excess of ammonia, and then excess of acetic acid. After simmering gently for half an hour the calcium oxalate is filtered off, ignited, and weighed as carbonate. The phosphoric acid is then determined, exactly as in the citric-oxalic-magnesium method of phosphate analysis already described—except that the operation is conducted all through in solutions of very small bulk. The sum of the lime and phosphoric acid deducted from the weight of the ammonium acetate precipitate will give the ferric oxide and alumina. The iron is determined by precipitating the total filtrates and washings from the precipitation and reprecipitation of the ammonium magnesium phosphate with ammonium sulphide. If allowed to stand for an hour or two at a temperature of about 80°C., the precipitate settles well, and may be rapidly filtered, washed with hot water to which a little ammonia and ammonium sulphide are added, ignited strongly and weighed as Fe_2O_3. The alumina is obtained by difference. The method is tedious, but accurate.

Modified Glaser Method.

The following method, modified from that of Glaser (which originally, but incorrectly, assumed a constancy of composition of the precipitate of mixed phosphates) is somewhat shorter, and gives results identical with those obtained by the method just described.

Four grams of the phosphate are treated with about 25 c.c. of strong hydrochloric acid and evaporated to dryness. The residue is taken up with 10 c.c. of strong sulphuric acid, about an equal bulk of water being cautiously added. After digestion in a water-bath for about ½ hour, the cake of calcium sulphate is well broken up by stirring with a glass rod, and the whole contents of the beaker are washed into a 200 c.c. flask with ordinary strong alcohol (methylated spirit), and allowed to remain for an hour with frequent shaking. The contents are then made up (with spirit) to 200 c.c., again well shaken and filtered rapidly. Of the clear filtrate, 100 c.c. (=2 grams of the sample) are evaporated in a glass or porcelain basin until the residue fumes and begins to 'char,' when it is washed with a little hot water into a beaker and mixed with sufficient bromine water to make it strongly orange-coloured. After standing for half an hour, the liquid is heated nearly to boiling and precipitated with slight excess of ammonia, kept in a water-bath for half an hour, and made slightly acid with acetic acid. The precipitate (which, under these conditions, contains only phosphoric acid, ferric oxide, and alumina) is filtered off, washed with a slightly ammoniacal 20 p.c. solution of ammonium nitrate, dried, ignited, and weighed. It is then dissolved in a little hydrochloric acid, 1 gram of citric acid is added to the solution, which is then made ammoniacal, and the phosphoric acid determined by precipitation with magnesium mixture. The total bulk of fluid should be kept within about 100 c.c. In this case, the precipitate of ammonium magnesium phosphate does not need re-solution and re-precipitation, seeing that no oxalate is present. The iron is precipitated from the filtrate with ammonium sulphide, as in the preceding process, and the alumina is arrived at by difference.

Analysis of Superphosphate, Dissolved Bones, &c.

'Moisture' is conventionally determined by simply drying to constancy at 100°C. The result should, in such cases, be stated as 'moisture' (*i.e.* loss at 100°C.), because the figure obtained is not moisture in the true sense, since it includes a varying quantity of water of hydration. True moisture can only be determined by drying to constancy *in vacuó* over sulphuric acid. The result in that case should be stated as 'true moisture' (*i.e.* loss *in vacuó*).

Determination of Soluble Phosphate.

Formerly in England, and still in America, solubility was determined by fractional exhaustion with successive small quantities of cold water (with or without a final exhaustion with hot water). On the continent of Europe it has long been usual to dissolve in a large bulk of water at one operation. The former method usually extracted somewhat more phosphoric acid than the latter, since some interaction occurs on dilution between the dissolved phosphoric acid and the 'insoluble' phosphate. As this depends upon the chemical composition of the original phosphate, and also on the degree of dilution, the differences in the results obtained by the two methods of extraction are variable—being sometimes negligible, but occasionally serious.

The following method of extraction of soluble phosphate, adopted at a meeting of the International Congress of Applied Chemistry, is now usually adopted in England, and is the method officially laid down in 1908 by the Board of Agriculture for use under the Fertilisers and Feeding Stuffs Act:—

> 'In the case of superphosphates, dissolved bones and similar substances, 20 grams of the sample shall be continuously agitated for 30 minutes in a litre flask with 800 c.c. of water. The flask shall then be filled to the mark, and again shaken, and the contents shall be filtered.'

The mode of determination of phosphate in the water solution thus obtained is officially prescribed as follows:—

> '50 c.c. of the filtrate shall be boiled with 20 c.c. of concentrated nitric acid, and the phosphoric acid shall be determined by the molybdate method prescribed below.'

Official Molybdate Method (Board of Agriculture, 1908),

'To the solution, which should preferably contain from 0·1 to 0·2 gram of phosphoric oxide (P_2O_5), 100 to 150 c.c. of molybdic acid solution prepared as described below, or an excess of such solution, *i.e.* more than is sufficient to precipitate all the phosphoric

oxide present in the solution, shall be added, and the vessel containing the solution shall be placed in a water-bath maintained at 70° for 15 minutes, or until the solution has reached 70°. It shall then be taken out of the bath and allowed to cool, and the solution shall be filtered, the phospho-molybdate precipitate being washed several times by decantation, and finally on the paper with 1 p.c. nitric acid solution. The filtrate and washings shall be mixed with more molybdic acid solution and allowed to stand for some time in a warm place in order to ascertain that the whole of the phosphoric oxide has been precipitated.

'The phospho-molybdate precipitate shall be dissolved in cold 2 p.c. ammonia solution, prepared as described below, and about 100 c.c. of the ammonia solution shall be used for the solution and washings. 15 to 20 c.c. of magnesia mixture prepared as described below, or an excess of such mixture, *i.e.* more than sufficient to precipitate all the phosphoric oxide present, shall then be added drop by drop, with constant stirring. After standing at least 2 hours with occasional stirring, the precipitate shall be filtered off, washed with 2 p.c. ammonia solution, dried, and finally weighed as magnesium pyrophosphate. The filtrate and washings shall be tested by the addition of more magnesia mixture.

'(*e*) *Preparation of molybdic acid solution.*

'The molybdic acid solution shall be prepared as follows:—

'125 grams of molybdic acid and 100 c.c. of water shall be placed in a litre flask, and the molybdic acid shall be dissolved by the addition, while the flask is shaken, of 300 c.c. of 8 p.c. ammonia solution, prepared as described below. 400 grams of ammonium nitrate shall be added, the solution shall be made up to the mark with water, and the whole added to 1 litre of nitric acid (sp.gr. 1·19). The solution shall be maintained at about 35° for 24 hours and then filtered.

'(*f*) *Preparation of magnesia mixture.*

'The magnesia mixture shall be prepared as follows:—

'110 grams of crystallised magnesium chloride and 140 grams of ammonium chloride shall be dissolved in 1300 c.c. of water. This solution shall be mixed with 700 c.c. of 8 p.c. ammonia solution, and the whole shall be allowed to stand for not less than three days and shall be then filtered.

'(*g*) *Preparation of the ammonia solutions.*

'The 8 p.c. ammonia solution shall be prepared as follows:—

'One volume of ammonia solution of sp.gr. 0·880 shall be mixed with three volumes of water. This solution shall then be adjusted by the addition thereto of more strong ammonia solution or water as required until the sp.gr. of the solution is 0·967.

'The 2 p.c. ammonia solution shall be prepared as follows:—

'One volume of 8 p.c. ammonia solution shall be mixed with three volumes of water.'

The soluble phosphate may be determined equally well by applying to 100 c.c. of the water extract, obtained by the official method of extraction (=2 grams of the original superphosphate) the oxalic-citric-magnesium process as described for raw mineral phosphates, omitting the evaporation to dryness; but in disputed cases in which litigation may arise, the molybdate method should be used.

Both 'soluble phosphate' and 'insoluble phosphate' in England are always stated in terms of tricalcium phosphate. On the Continent, it is usual to state them in terms of P_2O_5, with or without a statement of the equivalent $Ca_3P_2O_8$. The 'insoluble' phosphate is estimated by determining the 'total' phosphate and deducting from it the soluble phosphate.

Determination of Total Phosphate in Fertilisers.

This may, in most cases, be carried out by the methods already described for the analysis of raw mineral phosphates, materials containing much organic matter being first incinerated.

The official method prescribed in England under the Fertilisers and Feeding Stuffs Act, however, which should be adhered to in disputed cases, is the molybdate method, already described under soluble phosphate.

The official prescription of the Board of Agriculture for determination of total phosphate in fertilisers is as follows:—

> 'A weighed portion of the sample, in which portion, if necessary, the organic matter has been destroyed by ignition and the silica removed by appropriate means, shall be dissolved in nitric acid and boiled, the solution being made up to a definite bulk. The phosphoric acid shall be determined in an aliquot part of the solution by the molybdate method prescribed' (*see* above).

Reverted Phosphate.

The 'reverted' phosphate in superphosphate may be determined as follows: 2 grams of the sample are stirred up in a beaker with successive quantities of 50 c.c. of water, each portion, after settling, being decanted off through a filter. The water-soluble phosphate having been thus approximately removed, the matter on the filter is washed back into the beaker with a little water, and the undissolved matter is treated with either neutral or ammoniacal ammonium citrate solution. In America, neutral citrate is used, made by dissolving 185 grams of citric acid, neutralising with ammonia (using alcoholic solution of coralline as indicator), and making up to 1 litre. In France, a strongly ammoniacal solution is used, made by dissolving 400 grams in 1 litre of ammonia of sp.gr. 0·920.

In the American method, the water-insoluble residue referred to is digested with 100 c.c. of (neutral) citrate solution for half an hour with frequent shaking. In the French method, it is digested with 100 c.c. of (ammoniacal) solution for 12 hours, agitating occasionally during the first hour.

The matter undissolved by the citrate solution is filtered off, washed, ignited, and dissolved in hydrochloric or nitric acid and the phosphoric acid determined in it. The difference between water-soluble phosphate and total phosphate gives the insoluble (including reverted) phosphate. The difference between this and the phosphate undissolved by citrate solution is taken as 'reverted' phosphate.

Analysis of Basic Slag.

In the analysis of basic slag, it is now usual to determine (*a*) the percentage of 'fine meal,' (*b*) the percentage of total phosphoric acid, and (*c*) the percentage of phosphoric acid soluble in a 2 p.c. solution of citric acid.

Fine meal.—This is determined by sifting a given weight of the sample through a sieve made of brass gauze, having approximately 10,000 apertures per square inch, of the make known as 'Amandus Kahl, No. 100 E, Hamburg,' and weighing the residue.

As the size of the apertures depends upon the gauge of the wire, the use of any other make or pattern of gauge is a possible source of discrepancy. In well-ground slag from 80 to 90 p.c. should pass through the sieve. This is called the percentage of 'Fine meal.'

The *total phosphoric acid* may be determined as in mineral phosphates or as in other fertilisers.

An excellent method for slag, however, giving (by an admitted balance of errors) results identical with those of the molybdic process, is as follows: Treat 2 grams of the slag with strong hydrochloric acid and evaporate to dryness. Take up with 15 c.c. of hydrochloric acid and 25 c.c. of water, adding 20 grams of powdered citric acid. The silica is filtered off and washed, and the filtrate and washings (measuring about 170 c.c.) are cooled, a large excess of magnesium mixture is added and about 50 c.c. of strong ammonia. The liquid is stirred continuously for 15 or 20 minutes by aid of a mechanical stirrer, and allowed to stand with occasional stirring for 2 hours. The precipitate is filtered off, dried, ignited, and weighed as $Mg_2P_2O_7$.

N.B.—This process is largely in use on the Continent, without observance of the initial precaution of evaporating the acid solution to dryness to remove soluble silica. If the slag be merely digested with acid and the liquid filtered and precipitated without having been evaporated to dryness, the results may be seriously in excess of the truth. This has been pointed out by several investigators, but is not yet well recognised.

The phosphate soluble in 2 p.c. solution of citric acid is determined, according to the method prescribed in the official directions of the Board of Agriculture:—

'*Phosphate soluble in 2 p.c. citric acid solution.*

'5 grams of the sample shall be transferred to a stoppered bottle of about 1 litre capacity. 10 grams of pure crystallised citric acid shall be dissolved in water, the volume shall be made up to 500 c.c., and the solution shall be added to the weighed portion of the sample in the bottle. To lessen the possibility of caking, the portion of the sample in the bottle may be moistened with 5 c.c. of alcohol or methylated spirit before the citric acid solution is added; and in that case the volume of the citric acid solution shall be 495 c.c. instead of 500 c.c. The bottle shall be at once fitted into a mechanical shaking apparatus, and shall be continuously agitated during 30 minutes. The solution shall then be filtered through a large "folded" filter, the whole of the liquid being poured on the paper at once. If not clear, the filtrate shall be again poured through the same paper.

'50 c.c. of the filtrate shall be taken and the phosphoric acid shall be determined by the molybdate method prescribed.'

It may be added that 100 c.c. of the solution (=1 gram of sample) can be used equally well for the molybdate determination.

The phosphate in the citric acid solution of the slag is frequently estimated by direct precipitation with magnesium mixture after adding a large excess of ammonium citrate. The results, however, are inaccurate (being too high) unless the citric acid solution of the slag is first evaporated to dryness with hydrochloric acid to eliminate soluble silica. If this precaution be taken, the results compare well with those of the molybdate process—which, on the whole, is quicker, and therefore preferable.

Analysis of Potash Salts.

Some commercial potash salts are of complex constitution, others are approximately simple salts. The methods of determining such constituents as calcium, magnesium, chlorine, &c., do not differ from those ordinarily employed in inorganic analysis, but the essential determination, namely, that of potash, may be described. Broadly speaking, two methods are in use, namely, the perchloric acid method and the platinum chloride method. The perchloric acid method is little used in this country, but is recommended as an alternative method, presumably for factory purposes, by the chemists of the German Potash Syndicate.

Perchloric acid method. Ten grams or upwards of the salt are dissolved in water acidified with hydrochloric acid, and the sulphuric acid is precipitated with a minimum quantity of barium chloride solution. The liquid is made up to 500 c.c. and filtered, and an aliquot part equivalent to about ½ gram of the sample is evaporated in a porcelain basin with 5 or 6 c.c. of perchloric acid, until the odour of hydrochloric acid has disappeared and fumes of perchloric acid begin to form. The residue is allowed to cool, and is washed with 20 c.c. of strong alcohol containing 0·2 p.c. of perchloric acid, being thoroughly disintegrated. This washing is repeated several times, the crystals being brought on to a filter and finally washed with a small quantity of pure alcohol. The filter and its contents are dried at a temperature of 120° to 130°, and weighed. The crystals consist of $KClO_4$.

Platinum chloride method. The following are the details of the method for determining potash in potash salts officially prescribed in England in 1908 for use under the Fertilisers and Feeding Stuffs Act:—

'Determination of Potash.

'(*a*) *Muriate of potash free from sulphates.*

'A weighed portion of the sample (about 5 grams in the case of concentrated muriate of potash or 10 grams in the case of low-grade muriate) shall be dissolved in water, the solution shall be filtered if necessary and made up to 500 c.c. To 50 c.c. of the solution, placed in a porcelain basin, a few drops of hydrochloric acid shall be added, and also 10 c.c. or 20 c.c. (according to whether the portion weighed was 5 grams or 10 grams) of a solution of platinum chloride containing 10 grams of platinum per 100 c.c. After evaporation

to a syrupy consistency on a water-bath, the contents of the basin shall be allowed to cool and shall then be treated with alcohol of sp.gr. 0·864 being washed by decantation until the alcohol is colourless. The washings shall be passed through a weighed or counterpoised filter paper, on which the precipitate shall be finally collected, washed with alcohol as above, dried at 100°, and weighed.

'The precipitate is to be regarded as K_2PtCl_6.

'(*b*) *Salts of potash containing sulphates.*

A weighed portion of the sample (about 5 grams in the case of concentrated sulphate of potash or 10 grams in the case of kainit or other low-grade salts) shall be boiled with 20 c.c. of hydrochloric acid and 300 c.c. of water in a half-litre flask. Barium chloride solution shall be cautiously added, drop by drop, to the boiling solution until the sulphuric acid is completely precipitated. Any slight excess of barium shall be removed by the addition of the least possible excess of dilute sulphuric acid. The liquid (without filtration) shall be cooled and made up to 500 c.c. A portion shall then be filtered, and 50 c.c. of the filtrate shall be treated as in paragraph (*a*), 10 c.c. or 20 c.c. of platinum chloride solution, as the case may be, being used.'

(In calculating the results, international atomic weights are used, including Seubert's atomic weight for platinum, which, in the international table for 1911, is given as 195·2.)

The following is the method prescribed in 1908, under the Fertilisers and Feeding Stuffs Act, for the determination of potash in guanos and mixed fertilisers:—

'*Potash in guanos and mixed fertilisers.*

'Ten grams of the sample shall be gently ignited in order to char organic matter, if present, and shall then be heated for 10 minutes with 10 c.c. of concentrated hydrochloric acid, and finally boiled with 300 c.c. of water. The liquid shall be filtered into a half-litre flask, raised to the boiling-point, and a slight excess of powdered barium hydrate shall be added. The contents of the flask shall be cooled, made up to 500 c.c. and filtered. Of the filtrate, 250 c.c. shall be treated with ammonia solution and excess of ammonium carbonate, and then, while boiling, with a little powdered ammonium oxalate, cooled, made up to 500 c.c., and filtered. Of the filtrate, 100 c.c. are to be evaporated in a platinum dish, and the residue heated, first in the air-bath and then very gently over a low flame, till all ammonium salts are expelled, the temperature being carefully kept below that of low redness. The residue shall be treated with hot water, filtered, if necessary, and the potash shall be determined in the filtrate as in paragraph (*a*)" (*see* above).

DETERMINATION OF NITROGEN IN FERTILISERS.

Nitrogen was formerly determined by the soda-lime combustion process which was modified by Ruffle (Chem. Soc. Trans. 1881, 87), so as to be also applicable to mixtures containing nitrates by means of introducing into the soda lime an admixture of sodium thiosulphate. The soda-lime process has now, however, been almost universally superseded by Kjeldahl's moist sulphuric acid combustion process, modified and improved by the successive labours of many investigators In its present form it is one of the most accurate and reliable processes at the disposal of the analyst. It cannot be more clearly or concisely described than by quoting the directions laid down for its use in connection with the Fertilisers and Feeding Stuffs Act in the official regulations of the Board of Agriculture (1908):—

'The presence or absence of nitrates must first be ascertained.

'*Nitrogen in absence of nitrates.*

'A weighed portion of the sample shall be transferred to a Kjeldahl digestion flask; 10 grams of potassium sulphate and 25 c.c. of concentrated sulphuric acid shall be added, and the flask shall be heated until a clear liquid, colourless, or of light straw colour, is obtained. The operation may be accelerated by the addition of a small crystal of copper sulphate or a globule of mercury to the liquid in the digestion flask.

'The quantity of ammonia shall be determined by distillation into standard acid after liberation with alkali, and, where mercury has been used, with the addition also of sodium or potassium sulphide solution.

'*Nitrogen in mixed fertilisers when nitrates are present.*

'A weighed portion of the sample shall be transferred to a Kjeldahl digestion flask; 30 c.c. of concentrated sulphuric acid, containing 1 gram of salicylic acid, shall be added, and the flask shall be shaken so as to mix its contents without delay. The shaking shall be continued at intervals during 10 minutes, the flask being kept cool, and then 5 grams of sodium thiosulphate and 10 grams of potassium sulphate shall be added. The flask shall be heated until the contents are colourless or nearly so. Copper sulphate or mercury may be used as above described.

The quantity of ammonia shall be determined as above prescribed.'

The quantity of material operated upon will vary according to its nature. In the case of materials rich in nitrogen, from 1 gram to 1·5 grams may be operated upon. On the other hand, in the case of materials composed chiefly of inorganic matter, and containing only small quantities of nitrogen—like low quality dissolved bone compounds—as much as 5 or 6 grams may be conveniently operated upon. It is usually convenient to make two simultaneous experiments on different quantities of the material, such as 1 gram and 1·5 grams, or 1·5 grams and 2 grams. The larger the quantity of material that can be satisfactorily dealt with, the less, obviously, is the multiplication of experimental error. Duplicate results, in careful hands, should differ by no more than a few units in the second place of decimals, when expressed as percentage of nitrogen in the material under examination.

It is pointed out in the regulations that all the materials used in either of the methods described must be examined as to their freedom from nitrogen, by means of a control experiment carried out under similar conditions with the

same quantities of the reagents which are employed in the actual analysis, 1 gram of pure sugar being substituted for the weighed portion of the sample. The quantity of standard acid neutralised in the control experiment—which should be small if the materials are good—must be deducted from the total quantity of acid found to have been neutralised in the distillation of the sample. The observance of this precaution is of vital importance, seeing that small quantities of nitrogen compounds are frequently found even in sulphuric acid sold as pure for analysis; while traces of nitrates or nitrites may be present in sodium hydroxide.

In the above described modification of the Kjeldahl process for mixtures containing nitrates—due originally to Jodlbauer—phenol may be used, if desired, in place of salicylic acid, and 1 gram of zinc-dust may be used in place of the 5 grams of sodium thiosulphate. Zinc-dust, like the other materials, may contain traces of nitrogen, and must be carefully examined by being included with the other materials in a 'blank' experiment.

In the case of ammonium sulphate or other material containing nitrogen in the form of ammonium salts only (other than ammonium nitrate), the nitrogen may be determined by simple distillation with alkali.

Determination of nitrogen in sodium nitrate or in saltpetre. This may be carried out by several methods. One of the most convenient is the Ulsch method, which in the regulations of the Board of Agriculture is described as follows:—

> 'One gram of the sample shall be placed in a half-litre Erlenmeyer flask with 50 c.c. of water. 10 grams of reduced iron and 20 c.c. of sulphuric acid of 1·35 sp.gr. shall be added. The flask shall be closed with a rubber stopper provided with a thistle tube, the head of which shall be half filled with glass beads. The liquid shall be boiled for 5 minutes, and the flask shall then be removed from the flame, any liquid that may have accumulated among the beads being rinsed back with water into the flask. The solution shall be boiled for 3 minutes more, and the beads again washed with a little water. The quantity of ammonia shall then be determined as above prescribed. (*See Nitrogen in absence of nitrates.*)
>
> 'In cases in which the proportion of nitrates is small, a larger quantity of the sample shall be taken.'

General observations as to preparing samples for analysis. In the case of all samples, whether of fertilisers or of raw materials for use in their manufacture, it is obviously important to obtain a thoroughly representative portion for analysis. To this end it is usual, in the case of powdered fertilisers in dry or moderately dry condition, to pass the sample through a sieve, the perforations of which are about 1 mm. in diameter, pulverising the portions at first retained on the sieve—either in a mortar or, better, in a suitable mill—until they pass through. Adventitious materials which cannot be conveniently crushed, such as fragments of metal sometimes found in basic slag, must be removed and weighed, and subsequently allowed for in calculating the results of the analysis. Some materials, like shoddy, wool waste, or hair, cannot be powdered, but as a rule they can be passed through a shredding machine; or, if this is not possible, they must be finely cut up by hand. Some moist fertilisers do not admit of being passed through a sieve, and in dealing with these the analyst must use his discretion as to the best mode of obtaining an average sample. Crystalline or saline materials, like ammonium sulphate, potassium chloride, kainit, or sodium nitrate, are best prepared by mixing and rapidly grinding in a stoneware mortar, the portion reserved for analysis being especially finely ground. In the case of many moist materials, especially fibrous materials like shoddy wool waste, or rough fish guano, moisture is inevitably lost during the preparation of the sample. It is therefore necessary to separately determine the moisture in a large average portion of the original material before proceeding to pulverise the remainder. The moisture must also be determined in the fine material as prepared for analysis, and the results of the analysis recalculated so as to represent the percentages present in the sample in its original moist condition. In the case of raw mineral phosphates, it is usual to determine the moisture in a rough sample separately taken for this purpose, and to conduct the rest of the analysis on a separately prepared fine portion, after drying the latter at 100°—the results being returned on the dry basis, with a simple statement at the foot of the analysis of the percentage of moisture in the rough sample. But in the case of almost all other materials, the results of the analysis are returned as percentages of the material in its original moist condition. B. D.

FERULIC ACID. *m. Methoxy-p-hydroxy-cinnamic acid* $C_6H_3\begin{cases}CH:CH\cdot CO_2H & (1)\\ -OCH_3 & (3)\\ OH & (4)\end{cases}$. Occurs in asafœtida resin (Hlasiwetz and Barth, Annalen, 138, 64); in opopanax (Tschirch and Knilt, Arch. Pharm. 1899, 256), and in the resin of the black fir (Bamberger, Monatsh. 12, 441). The alcoholic extract of asafœtida resin is precipitated with lead acetate, and the precipitate, consisting of lead ferulate, is decomposed with sulphuric acid. It has been prepared artificially by means of Perkin's reaction by heating together vanillin, acetic anhydride, and dry sodium acetate, and decomposing the acetylferulic acid thus formed with potash (Tiemann and Nagai, Ber. 1878, 647); also by treating the methyl ether of *p*-amino-*m*-coumaric acid with sodium nitrite and decomposing the diazo-compound thus produced with water (Ulrich, J. 1885, 2093; *cf.* D. R. P. 32914; Frdl. i. 588). Rhombic needles, melting at 168°-169°, almost insoluble in cold water, readily soluble in alcohol, less soluble in ether (Tiemann and Nagai, Ber. 1876, 416). The solution gives with lead acetate a yellow flocculent precipitate, with ferric chloride a yellowish-brown precipitate, reduces silver nitrate and Fehling's solution on warming. Fusion with caustic potash converts it into acetic and protocatechuic acids. Sodium amalgam reduces it to hydroferulic acid $C_{10}H_{12}O_4$.

FETTBOL *v.* BOLE.

FIBRIN *v.* BLOOD and PROTEINS.

FIBRINOGEN *v.* BLOOD and PROTEINS.

FICHTELITE. Fichtelite occurs together

with retene in the turf beds of Redwitz in the Fichtel Mountains, and is found in the fossil stems of the sporadic bog-fir, *Pinus pumilio* (Haenke). It was found by Bamberger on the high-lying turf moor, near Rosenheim in Upper Bavaria. It occurs on the stumps of fossil pine-trees which project above the surface of the turf in the shape of a white efflorescence or crystals. It is easily isolated by extracting the wood with petroleum spirit, from which it separates on concentration in large crystals. From alcohol it crystallises in glassy prisms. Bamberger's experiments show that the formula $C_{40}H_{70}$, proposed by Clark (Annalen, 103, 236), is inadmissible. Its vapour density is 8·6; it contains 87 p.c. of carbon and 12·9 p.c. of hydrogen. Hence its formula is $C_{18}H_{32}$. It boils at 355·2° under 719 mm. Derivatives of fichtelite are very difficult to obtain, owing to the great stability of this singular hydrocarbon. It can be distilled over red-hot lead oxide without decomposition. When fichtelite is heated with iodine, hydriodic acid is given off and a syrupy yellow liquid is left. On distillation under 270 mm. pressure, the bulk goes over at 290°–295° as a thickish liquid, nearly colourless, and possessing a splendid blue-violet fluorescence. This body is *dehydrofichtelite*, differing from fichtelite in having two atoms of hydrogen less (E. Bamberger, Ber. 1889, 635–637, 3364). It is best separated from retene by repeatedly recrystallising from a mixture of alcohol and ether; it forms long prismatic crystals, melting at 46°. The mother liquors yield, on further evaporation, first retene and finally a brown soft mass, with a strong smell of vanilla. Vapour-density determinations by V. Meyer's method, at 440°, show that it has the formula $C_{18}H_{30}$. Dehydrofichtelite is identical with retenedodecahydride. Fichtelite is, in all probability, *perhydroretene* (Bamberger and Strasser, Ber. 1889, 3361; also L. Spiegel, *ibid.* 3069).

Fichtelite is acted on extremely slowly when boiled with fuming sulphuric acid, potassium dichromate, and sulphuric acid, or a 10 p.c. solution of potassium permanganate; but when treated with chromic acid in glacial acetic acid solution it seems to be oxidised to carbonic acid. It is not acted on by cold fuming nitric acid, but when boiled with nitric acid of sp.gr. 1·32 it yields oxalic acid. Bromine acts on it very readily, but the products could not be obtained free from unchanged hydrocarbon (C. Hell, Ber. 1889, 498–502; J. Soc. Chem. Ind. 1889, 382; Trommsdorff, Annalen, 21, 126; Bromeis, *ibid.* 37, 304; Clark, *ibid.* 103, 236).

For a review of the literature of fichtelite, *see* A. Schmidt, Centralbl. Min. 1901, 519. The monoclinic crystals of fichtelite are of interest in showing the same hemimorphic symmetry as crystals of tartaric acid and cane-sugar (H. Böckh Földtani Közlöny, Budapest, 1904, 34, 369), This is confirmed by F. Pizák and V. Rosicky (Zeitsch. Kryst. Min. 1908, 44, 332), who describe crystals from pine logs in a peat bog at Borkovic, Bohemia. These crystals have the composition $C_{18}H_{32}$, the molecular weight being determined by the cryoscopic method in benzene as 254·2; m.p. 46°; sp.gr. 1·01. Oxidation with chromic acid in an acetic acid solution yielded two acids, the silver salts of which are $C_{15}H_{20}O_6Ag$ and $C_3H_5O_3Ag$. L. J. S.

FICOCERYLIC ACID $C_{12}H_{25}COOH$. m.p. 57°, is obtained from the wax of the wild fig-tree.

FIG. *Ficus carica* (Linn.). Many varieties are known, varying greatly in size of fruit—from 6 or 7 grams to 80 grams each—the average weight of the fresh ripe fruit being about 35 grams.

According to Colby (Reports of the Agric. Exp. Stat. California, 1892–1894), the average of 41 analyses of different varieties is—

Water	Sugar	Protein	Ash
78·9	15·6	1·4	0·6

The juice, amounting on the average to about 76 p.c. of the whole, contained 20·7 p.c. of sugar and 0·12 p.c. of free acid expressed as sulphur trioxide.

Balland (Rev. intern. falsif. 1900, 13, 92) found more water, less nitrogenous matter, and in addition about 0·28 p.c. fat, and 1·5 p.c. crude fibre.

Colby found the ash to have the following composition (mean of 3 analyses):—

K_2O	Na_2O	MgO	CaO	Mn_3O_4	Al_2O_3 & Fe_2O_3	P_2O_5	SO_3	SiO_2	Cl
55·8	2·4	5·6	11·2	0·2	2·2	12·8	3·9	4·3	2·0

Figs are eaten in the fresh, ripe state in districts where they are grown, but, for export, they are largely dried. The following is the average composition of dried figs (König):—

Water	Protein	Sugar	Free acid (as malic acid)	Fat	Other carbohydrates	Fibre	Ash
28·8	3·6	51·4	0·7	1·3	5·3	6·2	2·7

The seeds of dried figs, according to Balland (*l.c.*), contain—

Water	Protein	Fat	Carbohydrates	Fibre	Ash
7·7	12·0	24·6	23·4	29·8	2·5

Hotter (Zeitsch. Nahrungsm.-Unters. Hygiene u. Waarenk. 1895, 9, 1) found, in dried figs from Smyrna, 0·0015 p.c. of boric acid. Wittmann (Zeitsch. landw. Versuchs Oesterreich, 1901, 4, 131) found 0·83 p.c. pentosans in fresh, 3·8 p.c. in dried figs.

According to analyses by Paladino (Biochem. Zeitsch. 1910, 24, 263), the following represents the composition of green and dried figs:—

	Water	Protein	Fat	Sugar	Cellulose	Mucilage, etc.	Ash
Green figs, pulp	80·0	0·7	0·3	16·2	1·3	0·8	0·7
,, ,, skin	86·0	(?)	0·1	5·4	5·8	2·7	(?)
Dried figs . .	57·0	4·1	2·2	26·0	8·0	0·2	2·5

It thus appears that the proportion of water in dried figs varies greatly.

When figs are moistened with warm water containing tartaric acid, they speedily ferment and yield a wine. This is largely made in Algeria, and is used for adulterating grape wine. When fig wine is evaporated to a syrup and allowed to cool, it solidifies, after 24 hours, to a crystalline mass consisting chiefly of mannitol, but containing glycerol and small quantities of sugar and organic acids. Mannitol is present in fig wine to the extent of 6 or 8 grams per litre, whilst in grape wine its amount does not exceed a few decigrams per litre. This fact may be used

to detect fig wine as an adulterant of grape wine (Cables, Compt. rend. 1891, 122, 811).

The stems and branches of plants of the genus *Ficus* yield a viscid, milky juice containing caoutchouc or resinous substances resembling caoutchouc. *F. elastica* (Roxb.) is the species from which the largest proportion of this substance is obtainable. H. I.

FIG WAX *v.* WAXES.

FILBERT. The seed of *Corylus Avellana* (Linn.). The kernels have the following average composition (König):—

Water	Protein	Fat	Soluble carbohydrates	Crude fibre	Ash
7·1	17·4	62·6	7·2	3·2	2·5

These were evidently in the dried condition; as usually eaten, for dessert, filberts contain much more water. The essential oil of the leaves was examined by Haensel (Chem. Zentr. 1909, i. 1476), who found it present to the extent of 0·04 p.c. It is light brown in colour, solidifies at about 30°, contains 18 p.c. of palmitic acid, and a paraffin hydrocarbon melting at 49°. It had an acid value 60·4, ester value 24·6, and its sp.gr. (in the super-cooled liquid condition) was 0·8844 at 25°. H. I.

FILICIC ACID *v.* FILIX MAS.

FILITANNIC ACID *v.* FILIX MAS and TANNINS.

FILIX MAS. Male fern; *Rhizome filicis.* (*Racine de fougère mâle*, Fr.; *Farnwurzel*, Ger.) The rhizome of male fern, *Aspidium filix mas* (Swartz), has been a favourite anthelmintic medicine since the times of Theophrastus, Dioscorides, Pliny, and Galen. (For botanical characters, *v.* Woodville (Med. Bot. 271), Moore and Lindley (Ferns of Great Britain, 14–17), and Bentl. A. Trim. 300.)

The early chemical investigations of the rhizome, of which Pereira gives a summary (Mat. Med. 3rd ed. 2, 959), show that, besides the constituents common to plants, it contains a peculiar *green fixed oil*, *tannin*, and a crystalline compound, first analysed by Luck (J. 1851, 558) and named by him *filicic acid*. These constituents are all found in the ethereal extract or 'oil of male fern,' in which form alone the drug is made use of in medicine.

The green fixed oil is composed, according to Luck, of the glycerides of the non-volatile *filixolinic*, and the volatile *filosmylic acids*. A later examination by Katz (Arch. Pharm. 236, 655) shows that the oil consists of the glycerides of oleic, palmitic, and cerotic acids, the chief constituent being triolein. Luck also regards the tannin to be composed of two compounds, the one 'tannaspidic acid' insoluble, and the other 'pteritannic acid' soluble in ether. Malin, however (Annalen, 143, 276), shows that there exists but one form of tannin, which he isolates and names *filitannic acid*. This is a glucoside, breaking up through the agency of water (dilute acids) into a sugar and dark brick-red flocks of *filix red*, $C_{20}H_{14}O_{12}$. The latter compound, when treated with caustic potash, yields phloroglucin and protocatechuic acid. The tannaspidic acid of Luck was probably filix red.

Filicic acid is described by its discoverer as a light-yellow crystalline powder, melting at 161° (184·5°, Poulson). In water it is insoluble, in alcohol only slightly soluble; but ether, especially in presence of the green fixed oil, dissolves it readily.

By boiling the ethereal solution, filicic acid is readily converted into the lactone *filicin*, m.p. 125°, the formula of which is given as $C_{35}H_{40}O_{12}$; that of filicic acid being $C_{35}H_{42}O_{13}$ (Poulson, Chem. Zentr. 1891, ii. 673). By heating filicin with an aqueous solution of soda, phenol, phloroglucin and *filicinic acid* $C_{11}H_{14}O_4$ were obtained. The latter compound melts at 215°, and on oxidation yields dimethylmalonic acid (Boehm, Chem. Zentr. 1896, ii. 1036).

In addition to filicic acid, Boehm (*l.c.*; Annalen, 318, 245, 253; *ibid.* 329, 321, 338) has isolated from male fern extract the following substances: *albaspidin* $C_{31}H_{32}O_8$; *flavaspidic acid* $C_{24}H_{28}O_8$, which can be obtained in two forms, α- m.p. 92°, and β- m.p. 156°; *aspidinin*; *aspidinol*, consisting of bright-yellow crystals, m.p. 156°–161°; and *phloraspin* $C_{23}H_{46}O_8$, colourless crystals, melting at 211°, and giving a reddish-brown colouration with ferric chloride. A further compound, *aspidin*, was also obtained, but Haussmann (Arch. Pharm. 237, 544) has shown that this substance does not occur in *Aspidium filix mas* (Swartz), but in *Aspidium spinulosum* (Swartz), and that when detected in the commercial extract it owes its presence to the roots of the latter fern having been mistaken for those of the former, which they somewhat resemble.

Kraft (Chem. Zentr. 1902, ii. 533; 1903, i. 1090; Arch. Pharm. 242, 489) finds that good extracts of male fern contain on an average 3·5 p.c. filicic acid, 2·5 flavaspidic acid, 0·05 p.c. albaspidin, 0·1 p.c. aspidinol, 0·1 p.c. flavaspidin, 5 p.c. amorphous acid, and 6 p.c. filicinigrin. *Flavaspidin* resembles flavaspidic acid very closely; it is, however, less soluble in carbon disulphide. It melts at 199°, and is possibly the same compound as Boehm's phloraspin. The *amorphous acid*, to which Kraft gives the name *filmarone*, forms a brownish-yellow powder, melting at 60°, and to this substance Kraft attributes the anthelmintic action of the drug. The composition is represented by the formula $C_{17}H_{54}O_{16}$. The substance described as 'filicinigrin' appears to be only a mixture of decomposition products.

(For detection of filicic acid in cases of poisoning, *see* Bocchi, Chem. Zentr. 1896, ii. 1137.) A. S.

FILIX RED, FILOSMYLIC ACID *v.* FILIX MAS.

FILTER PUMPS. The filter pump is generally some form of dynamic air pump. Sprengel, in 1865 (Chem. Soc. Trans. 18, 9), showed how a very perfect vacuum could be obtained by the fall of mercury or other liquids, and Bunsen, in 1868 (Annalen, 148, 277), showed how the difference of pressure so obtained could be utilised in greatly improving the ordinary process of filtration.

This application has given a name to all these instruments, though they are applicable to nearly all the purposes for which any ordinary air pump or aspirator might be used. Many of them, with a continuous supply of falling liquid or of steam or other gas, under pressure, are almost automatic in their working, and far more convenient than any piston air pump.

The pumps used in laboratories are of three kinds:

1. Barometer or weight pumps.
2. Momentum or pulsation pumps.
3. Injection or pressure pumps.

1. Barometer pumps. Of these there are two varieties, the statical or Geissler pump, and the dynamic or Sprengel pump.

The Geissler pump was invented about 1855 by Geissler, and in it air is exhausted by the alternate emptying and filling with mercury of a vessel forming the upper part of a barometric column. It is simply an application of the Torricellian vacuum. Geissler used this pump in the production of his vacuum tubes, and since his time it has been modified and improved by many inventors: Töpler (Dingl. poly. J. 1862, 423), also Poggendorf, Mitscherlich, Pflüger, Joule, and others.

The Sprengel pump, in its simplest form, is a plain tube of small but uniform bore, and of a length rather greater than that of the barometric column of the liquid used in it. It is furnished with a side tube near its upper extremity. The continuous falling of the liquid, generally mercury or water, produces the exhaustive effect, which is slow at first, but can be made to give a more perfect vacuum than is possible by any other means. The improvements of the Sprengel pump have been chiefly towards quickening its action, and have been described by McLeod, Swan and Stearn, Gimingham, Weinhold, and others. Crookes' experiments on the radiometer and radiant matter were rendered possible by the use of the Sprengel pump, and in the manufacture of incandescent electric-lighting lamps these barometric pumps have had a considerable industrial application. The Sprengel pump, worked by water, was that used by Bunsen in his improved mode of filtration, and this application—the most important to the chemist—gave rise to the many inventions described below in this paper.

2. The momentum or pulsation pump. This was described by Jagn, in 1872 (Pogg. Ann. 148, 317). It consists of a plain tube of moderate length, with side tube near the upper end. In action, the soft indiarubber tube connecting the apparatus with the water supply (of a very moderate fall or pressure) is ingeniously made to act as a valve by which the water is alternately admitted and shut off. We have thus an action similar to that of the hydraulic ram, in which the momentum of a column of liquid comes into play. In the ram, water is raised in front by the momentum; in this pump, air is pulled in behind. Modifications of the Jagn pump have been described by Thorpe (Phil. Mag. 1872, 249), also by Foote, Linnemann, and O. Witt. As these pumps are intermittent in their action, they work more slowly than others which are continuous, and have been superseded by them.

3. Injector or pressure pumps. These consist of tubes of various forms, but generally furnished with a jet or narrow neck in front of a wider neck or expanding mouthpiece. Any liquid or gas under pressure, such as water or steam, may be used to work them, and in any position.

They are similar in principle and construction to the water pump (Fig. 1) described by James Thomson (B. A. 1852-3) or the Giffard steam injector, patented in 1858. The principle of the injector was, however, partially known long before. Hawksbee, in 1719, found that on blowing through a tube into a small box, the air escaping by another tube opposite the first, the pressure in the box became less than that of the atmosphere; and D. Bernouilli, in

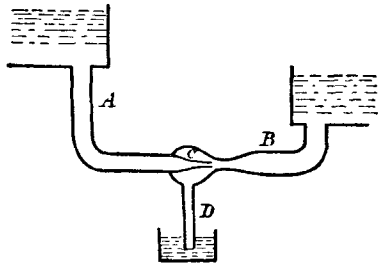


FIG. 1.

1738, found that water from a higher source flowing towards the wide end of a conical tube could lift water from a lower level through a side tube attached near the narrow part of the conical tube. Between 1830 and 1850, the steam-jet aspirator was used by Carson, G. Stephenson, and others. Clement and Desormes, in 1855 (Ann. Chim. Phys. 36, 69), showed that a light plate brought near a small orifice in the side of a reservoir of compressed air was attracted, and remained rapidly oscillating near the opening. This effect can be shown by blowing between the fingers against a piece of paper, or by blowing between two cards, as described in Weinhold's Physics, 312. All these experiments are examples of the passage of a fluid through an expanding mouthpiece, causing a diminished pressure as compared with that in front, which in each case is that of the atmosphere.

The first injector air pump for laboratory use was that of Christiansen, described in 1872 (Pogg. Ann. 196, 155). In Fig. 2, A is a piece of thick-walled indiarubber tubing, perforated at B by a hot wire, and constricted at C by a ring drawn over the tube. On inserting at B a short piece of bent glass tubing drawn out to a jet, and connecting the top end of A with the water supply under moderate pressure, air is drawn in through the bent tube, and a considerable vacuum obtained.

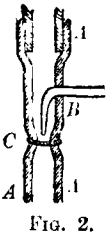


FIG. 2.

Other early forms of injectors were described by Lovett (Chem. News, May, 1874, 209) and Casa major (*ibid.* June 27, 1875, 33); and soon after these dates numerous forms were invented for the use of chemists, dentists, &c.

The experiments of W. Froude (B. A. 1875), though made for a different purpose, afford an excellent explanation of the action of injectors.

Froude showed that water under any head H (Fig. 3), passing through a contracted pipe, does not exert an excess of pressure on the converging surface, which it meets, as is frequently stated, but that the pressure is least at the contracted

part, as shown by the levels in the gauge glasses *a, b, c, d, e*. If the pipe be much contracted, the pressure can be still more reduced, so that if two cisterns, A and B (Fig. 4), be connected by such a contracted pipe, a portion of the pipe at C may be removed without the flow of the liquid being interfered with; the water rising in the cistern B only slightly below its level in A. At F, in the

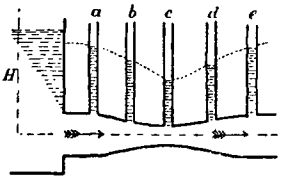


FIG. 3.

central line of the connecting pipe, the full head of pressure H is exerted, but there is practically no movement, while at C there is no pressure, but very rapid movement. The pressure and velocity of movement are therefore convertible and complementary, and the differences of pressure at any two points vary as the differences

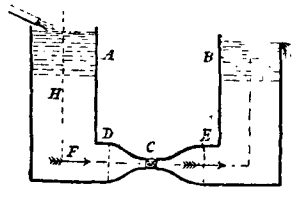


FIG. 4.

of the squares of the velocities at those points. In any given case the pressure observed, *plus* that which has been lost in producing velocity, is constant and equal to the total head of water H (Figs. 3, 4, 5). If we modify Froude's experiment and cut off the pipe at E (Figs. 4, 5), the pressure at E is simply the general pressure of the atmosphere, and all the pressure due to the head of water in A has been changed into velocity, but the velocity at C must be greater than the velocity at E by as many times as the sectional area of the pipe at C is contained in its area at E. The velocity at C being so much greater than at E, the pressure must be less, and therefore less than that of the atmosphere. The tube G (Fig. 5) may be regarded as a gauge to show the minus pressure, and if this gauge be supplied with mercury, the latter may rise to near the height of the barometer. In place of water or liquid under pressure, air, steam, or any gas under pressure may be used, and injector air pumps worked by steam have been proposed by Lovett, Kochinke, Teclu, and others.

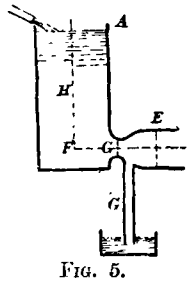


FIG. 5.

Injector air pumps, worked by water, may be classified:

(*a*) As in Figs. 6, 7, where the water enters by a jet placed over a constricted tube or neck, the air being drawn in on all sides round the jet of water. The ratio of the areas of the jet and neck in this form is generally 1 : 2, or their respective diameters 1 : 1·4.

(*b*) As in Fig. 8, where the jet and neck are continuous and the air enters on one side only.

(*c*) As in Fig. 9, where the general form is similar to (*a*), but the air enters by a very narrow jet and the water filling the body of the pump enters all round the jet.

These differences in construction are of little importance in the practical working of the instruments, but by altering the width of the

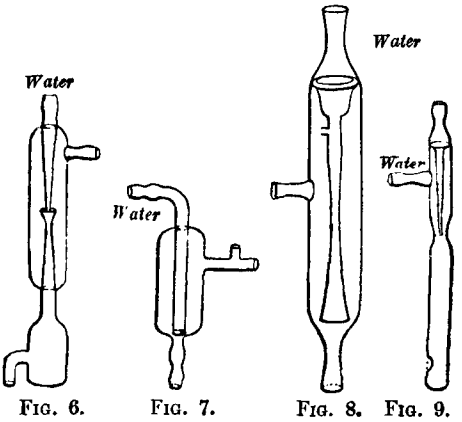


FIG. 6. FIG. 7. FIG. 8. FIG. 9.

apertures, pumps suited to different pressures can be obtained. Pumps with very narrow apertures work best with small quantities of water at very high pressures, whereas pumps with wider apertures require much more water at a low pressure. As the water passing through these instruments is practically a falling body, on multiplying the weight of water in pounds used per minute by its head or pressure in feet, we obtain in foot-pounds the power required to produce the exhaust in one minute's working of the pump. Compared in this manner, the low-pressure pumps are less efficient than those working at higher pressures.

In using these injectors, care should be taken to have a sufficient and constant water supply. The water tap turned full on should supply in one minute twice to three times the quantity required by the pump in the same time. In towns and large buildings, where many persons are using the water at different levels, the pressure is often very variable, and a reservoir of water under pressure is necessary. A simple form devised by the author is a strong iron bottle (or an iron boiler) capable of standing a greater pressure than is likely to be required, say up to or over 100 lbs. per square inch. This bottle A (Fig. 10) has one tube passing to the bottom connected by a T-piece with the water-supply pipe, and it may carry a pressure gauge if desired. The connection with the water tap may be made with lead pipe and soldered joints, or with sound rubber tubing encased in a double thickness of strong canvas sewn over it, the connections being well bound with copper wire. The bottle being air-tight and water-tight under pressure, and full of air when connected with

the supply pipe, the air cannot escape, but is compressed by the pressure of the water. Thus at 15, 30, or 45 lbs.' pressure the bottle becomes half, two-thirds, or three-fourths full of water, and with a variable pressure in the supply pipe keeps the pressure more constant, and maintains the supply for some time, depending on the size of the bottle or reservoir. Passing from this reservoir, the supply pipe is next led

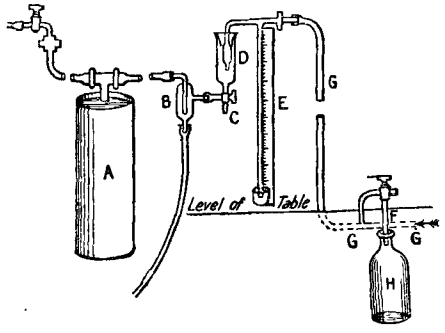


FIG. 10.

to the pump B, which may be conveniently fixed out of the way on a board against the wall behind the laboratory table. The board carries a barometric gauge to show the vacuum obtained.

Passing from the pump, the water used runs into the sink on the laboratory table, or if desired it may be connected with a box or drum provided with an overflow at a certain height, so as to give a blast of air under pressure suitable for general blowpipe work. The vacuum tube from the pump is connected by means of the tap C (Fig. 10) with the safety tube D, having a Bunsen valve fitted inside to the end of the vacuum tube, thence with the barometric gauge E and the laboratory vacuum tube G.

Fig. 11 shows in full size the tap C in Fig. 10, which is fitted to the bottom of the safety tube and to the laboratory vacuum tube at each working place on the tables F (Fig. 10). An ordinary good gas tap, which should be specially ground so as to be as air-tight as possible, has the little screw and washer at the bottom of the plug removed and a hole bored from C into the ordinary through hole of the tap, the latter being soldered up at one side at D, so that the hole is from the bottom to one side only, and the plug is then trimmed and reground. A piece of tubing, FF, is then soldered on to the body of the tap and a pointer, E, soldered on to the top of the plug to point which way it is open. When the plug is turned across in the ordinary position of a closed tap, it is closed to both A and B; when the pointer points to A, it is open towards A, and if towards B to B. The tube FF is fitted air-tight by means of a stopper in the bottle H (Fig. 10).

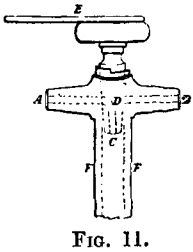


FIG. 11.

By means of these taps (devised by the author in 1883), one pump can do all the exhaustion work in an ordinary laboratory for a number of filtrations going on simultaneously. The pump is connected with a main pipe of soft lead tubing passing along or under the laboratory tables, and at each worker's place is a bottle like H (Fig. 10) fixed below the table, the tube FF from it rising above the table. One end of the tap, say A, is connected with the vacuum main pipe by soldered lead tubing; the other end of the tap is connected by a flexible tube with the filtering apparatus or other vessel to be exhausted.

In using this arrangement, all the vacuum supplied at B must come from the bottle below FF, and not from the main pipe, which is then shut off. When the vacuum is not required at B, the tap is turned towards A to raise the degree of exhaustion in the bottle. As these bottles are of half-gallon or 2·2 litres capacity, a moderate vacuum in one of them (say half to three-quarters the height of the barometer) is sufficient for a filtration on the small scale, and as there are a number of such bottles in the laboratory they form together a vacuum reservoir of some magnitude available at once without waiting. If well fitted, the taps retain the vacuum for several days. A lute made by dissolving indiarubber in vaseline at as low a temperature as possible is of good service for these taps and connections.

The author has made a series of comparative tests of the pumps in common use (J. Soc. Chem. Ind. 1887, 64–76). With a supply and pressure of water suited to each pump, and exhausting receivers of the above capacity, 2·2 litres, vacua corresponding to from half to three-quarters of the height of the barometer could generally be obtained in one minute's workings; such vacua are quite sufficient for ordinary filtrations.

As the apparent size of these instruments is somewhat misleading, the quantity of water used is the real test of size; pumps of the same construction but of different sizes would exhaust a receiver at different rates, but in proportion to the water used.

The table on p. 562 gives the results in brief of tests made with the pumps most frequently found in use; first, in exhausting a receiver of 2·2 litres capacity, and second, in blowing air, with the exhaust tube of the pump open to the atmosphere. The results of the first minute's working only are given, though the tests were carried on to 10 minutes. In each case, those pumps which worked best during the first minute continued to do so throughout, and came nearest to the height of the barometer at the end of the exhaustion.

The blowing power of each pump is also a test of its exhaustive power, as in blowing with the pump open to the atmosphere it is practically exhausting an infinitely large receiver.

Of the high-pressure pumps, those of Fischer, Bulk, Knecht, and Muencke's brass pumps give good results, and of the low-pressure pumps, which use more water, those of Arzberger and Zulkowsky, Finkener, and Körting, are good. Alvergniat's glass and brass pumps are intermediate in character, and work well through a considerable range of pressure.

Given abundance of water at sufficient pressure, the pumps which give the most rapid exhaustions are those of Finkener, Körting, Alvergniat, Arzberger, and Zulkowsky; but

TABLE OF THE FIRST MINUTE'S WORKING OF THE PUMPS.

Name of pump	(a) Exhausting the receiver of 2·2 litres capacity											(b) Blowing power			
	Water pressure in pounds per square inch										Ratio of volume of air pumped out to water used	Water pressure in lbs. per sq. inch	Litres per minute		Ratio of air to water
	5	10	15	20	25	30	35	40	45	50			Air blown	Water used	
	Vacuum obtained in one minute														
	mm.	mm.	mm.	mm.	mm.	mm.	mm.	mm.	mm.	mm.					
Alvergniat Frères (glass) (Fig. 6) . .	—	302	395	442	481	515	564	577	—	—	Varies from 0·27 to 0·29	40	5·90	6·32	0·93
„ „ (brass) . . .	—	182	240	322	385	426	452	468	—	—	„ 0·24 to 0·29	40	4·35	5·08	0·85
Arzberger and Zulkowsky (brass) [1] . .	221	286	374	468	530	—	—	—	—	—	„ 0·14 to 0·16	25	4·36	9·52	0·46
„ „ with outflow tube in lowest position	—	330	419	507	562	—	—	—	—	—	„ 0·14 to 0·16	20	4·51	10·8	0·42
„ „ in highest position	—	156	213	273	342	478	497	512	—	—	„ 0·17 to 0·28	40	3·90	5·44	0·79
Bendix (brass)	—	226	299	356	406	442	468	478	—	—	„ 0·22 to 0·25	40	4·65	5·92	0·79
Bulk (glass),[2] (Fig. 9)	—	160	226	286	338	395	426	458	—	—	„ 0·24 to 0·32	40	2·65	4·26	0·62
Finkener (glass) [3]	—	—	—	—	447	551	582	—	—	—	„ 0·21	35	6·38	8·24	0·77
Fischer (glass),[4] (Fig. 7)	—	203	247	286	322	380	408	419	—	—	„ 0·33 to 0·35	40	5·15	3·52	1·46
„ (brass, by Dreyer & Co.) . .	—	135	205	268	312	351	390	421	—	—	„ 0·35 to 0·54	40	3·24	2·26	1·48
„ (brass, by Desaga) . . .	—	226	261	364	390	416	439	491	—	—	„ 0·36 to 0·37	40	4·73	3·80	1·22
„ (brass, copy by ?) . . .	—	143	226	265	283	312	346	380	—	—	„ 0·30 to 0·40	40	2·90	2·75	1·05
Geissler (glass) [5]	—	117	162	179	205	234	252	307	329	—	„ 0·21 to 0·25	40	1·76	3·53	0·50
Knecht (brass)	—	—		161	252	278	286	296	299	—	„ 0·35 to 0·54	40	0·90	1·73	0·52
Körting (brass) [6]	195	333	426	499	546	582	—	—	—	—	„ 0·15 to 0·23	30	4·15	8·32	0·50
Mawson and Swan (No. 1 glass),[7] (Fig. 8)	—	182	239	273	320	331	439	458	—	—	„ 0·23 to 0·28	40	3·00	4·88	0·62
„ „ (No. 2 glass) [8] . .	—	138	179	202	247	289	432	447	—	—	„ 0·16 to 0·28	40	2·95	4·96	0·59
„ „ (No. 3 glass) [9] . .	—	130	192	229	266	309	335	376	—	—	„ 0·28 to 0·36	40	2·25	3·01	0·75
Muencke (No. 971 glass) . . .	—	276	338	395	429	458	486	—	—	—	„ 0·18 to 0·19	35	3·30	8·52	0·39
„ (No. 970 glass) . . .	234	307	398	473	515	—	—	—	—	—	„ 0·14 to 0·16	20	2·76	8·60	0·32
„ (No. 948 small brass) . .	—	—	—	—	—	356	390	413	432	458	„ 0·53 to 0·56	50	2·75	2·86	1·12
„ (No. 952 adjustable brass with three-way tap) . . .	—	—	—	356	426	486	507	535	—	—	„ 0·31 to 0·34	40	4·00	4·72	0·85

[1] Ann. d. Chem. u. Pharm. Bd. 1875, 176, p. 327. [2] Ber. d. deutsch. chem. Ges. 1876, p. 1871. [3] Winkler's Industrie Gaze, i. p. 23. [4] Dingl. poly. J. 1877, 221, p. 136 and 225, p. 342.
[5] Sent out about 1876. [6] Sent out about 1880. [7] Sent out about 1876. [8] Sent out about 1877. [9] Sent out about 1879.

where economy of water is desired, the high-pressure pumps ought, if possible, to be used. Though considered as machines doing work for the power put into them, none of these injectors is very perfect, yet they are exceedingly convenient, and it will be observed that all those tested give *at some particular* pressure in one minute's working sufficient vacua for filtrations and similar laboratory work.

In choosing an instrument for laboratory use, one should ascertain the average quantity of water per minute delivered by the fully open water tap and also the average pressure in the closed water pipes. The pump selected should require not more than half the quantity of water delivered by the open tap, and should work well at from half to two-thirds of the pressure in the closed pipes.

In recent years, there has been a great increase in the use of injectors for industrial purposes, including many chemical and mechanical applications.

Generally, the energy applied in injectors gives about 50 p.c. in real effective duty, but their low initial cost, absence of moving parts, and of metallic or corrodable surfaces, and above all the perfect control under which they can be applied and regulated, more than make up for the low percentage of duty. Thus they are ideal machines where ordinary pumps or exhausters are inadmissible, and are excellent as auxiliary agents to more complicated or permanent apparatus for improving the draught in furnaces, the ventilation in mines and workshops, and the conveyance or transfer of corrosive liquids and gases, and of mixtures of solids and liquids, such as ordinary sewage, and of mixtures of sand and water. The removal of ashes in steamships is most conveniently effected by this means.

Injectors are used to produce a blast for the division or spraying of liquids, as in the burning of liquid or semi-liquid fuels under boilers, the coating of large surfaces by spraying the paint over them, even where they are difficultly accessible. The spraying of water into the leaden chambers in the manufacture of sulphuric acid is found to be more efficient than the admission of steam.

Similarly, the exhaust obtained by injectors worked by air, steam, or water, is applied in the various methods of vacuum cleaning. These applications are well described in the book on The Transportation of Gases, Liquids, and Solids, written and published by Oskar Nagel, of New York, 1910. T. F.

FILTRATION is the operation of mechanically separating finely divided solids from their associated liquids by means of porous media.

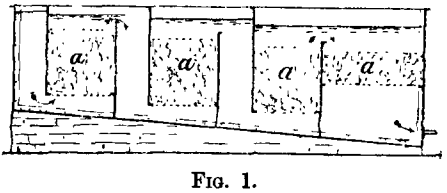


FIG. 1.

The media used may consist of loose material, such as sand; a compact body, such as biscuit pottery; or woven or felted materials, such as cloth, paper, and felt. It may be remarked, however, that the real filtering medium is often the layers of separated solids, the materials mentioned above only serving as convenient supports. A loose filtering medium is generally adopted where the proportion of liquid is relatively large and the solids of little value. The filter shown in Fig. 1 may be used for cleansing an effluent. Each compartment, *a*, is filled with wood-wool, kieselguhr, or similar material which is replaced when choked. Fig. 2 is a section of

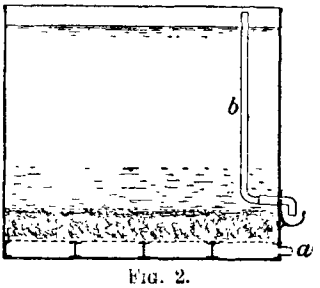


FIG. 2.

a filter in which the bed, 6–10 inches deep, is formed by means of layers of graded materials, as gravel, sand, coke, limestone, &c. The upper layer of (finest) material is retained in place by a covering of stout wire gauze or perforated metal, when the shovels of the workmen are removing the separated solids. By providing a movable basket with a bottom of gauze which may be lifted by means of a crane, an economy in handling is effected where labour is dear. This filter is intended for vacuum working by connecting the lower pipe opening *a* to a vacuum vessel and pump. The swinging pipe *b* enables the workman to remove rapidly the upper layers of liquid, which may become clear by subsidence. In filters of this type, where the solids are of no value, their removal is often accomplished by stirring the upper layers and running to waste the turbid liquor. The direction of the liquor current is often reversed for the same purpose. The ordinary domestic water filter, in which hollow cylinders of biscuit pottery are used as the filtering medium, is occasionally met with in a large form in chemical factories. To obtain suitable porosity, such filtering devices are made of clay mixed with finely divided combustible materials such as wood, cork, &c., which are burnt off in the process of firing. Filter stones are made on this principle, in which the layers are of varying porosity. Such stones replace filter cloths with economy, and are becoming very popular in colour and other chemical factories. The simplest filtering apparatus in which a woven fabric is used consists of a frame to which the fabric is secured. A wicker basket is sometimes used, and this arrangement is most convenient where the cake of material is to be folded in the cloth and squeezed in a press for the removal of more liquor. Washed graphite and similar materials are often separated in long and narrow canvas bags tied to spouts in the delivery channel from the washing apparatus. A simple form of vacuum filter, using a woven fabric or a disc of paper as a filtering medium, is shown in Fig. 3. It is made in stoneware, the perforated plate *b*

supporting the fabric and the vacuum pump being connected with the nozzle *a*.

Filtration may be carried out in centrifugal machines which are conveniently driven from below. The rotating basket is provided with a removable cage carrying the filtering cloth, which is bodily removed and replaced at each operation. Another system by which rapid filtration may be obtained with a small area of filtering surface consists in mounting the filter cloth on a perforated drum, as shown in the diagrammatic section (Fig. 4). The drum revolves about once a minute in a bath of the liquid to be filtered which is maintained at a constant level. The filtrate is removed from the inside of the drum under a vacuum of 10 or 12 inches of mercury, produced by connecting the hollow spindle of the drum with a vacuum vessel and pump. The deposited solids on the surface of the drum are washed by the water jets *b* and finally removed by the scrapers *c*.

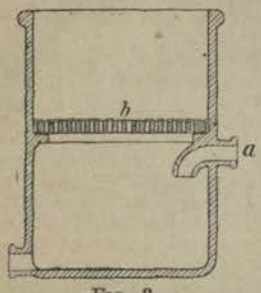


FIG. 3.

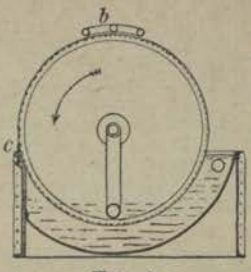
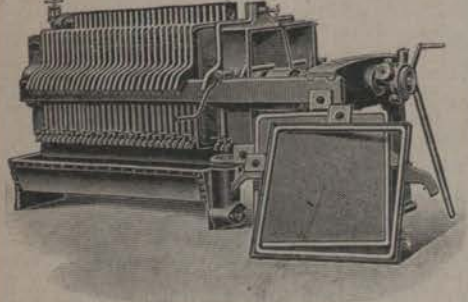


FIG. 4.

The most important apparatus for filtration is the filter press (Fig. 5)—a mechanical arrangement by which an enormous area of filtering surface may be provided in a very small space, with the additional advantage that the operation may be carried out under almost any conditions of pressure. A number of plates covered with filter cloth are put together in a frame to form a series of hollow spaces in which the liquor to be filtered is forced. The central area of each plate is provided with projections or ribs to support the filter cloth and to enable the liquid which has passed through the cloth to leave the press through a channel in the plate. The solid matter is retained in the hollow spaces, and is discharged in cakes by separating the plates. The hollow spaces between the plates are formed either by raised margins on the plates, *Recessed plate type* or *chamber press* (Fig. 6), or by means of distance frames, the width of which determines the thickness of cake formed, *Flush plate and distance frame type* or *frame press* (Fig. 7). The plates and frames are made of material suitable for the liquors to be treated, and may be of cast iron, gun-metal, aluminium, hard lead, wood, &c. Iron plates are sometimes covered with sheet tin, lead, zinc, or ebonite. Chamber presses are to be preferred where the solids do not form a solid cake, or where there is risk of choking the narrow channels leading to the



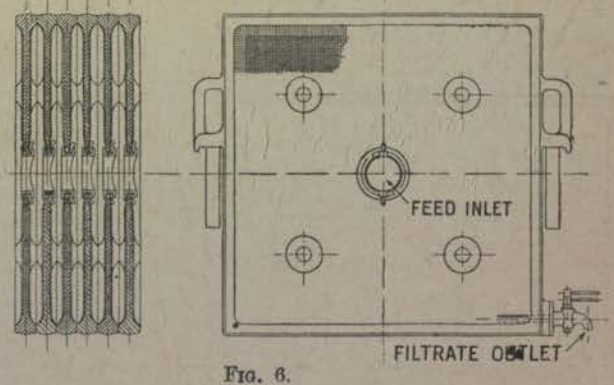


FIG. 6.

frames of the frame press. The pressure used and the thickness of cake are also determined by the character of the separated solids. With slimy solids, a thin plate and a low pressure are desirable; the cake may be ½ inch thick and the pressure may be that produced by placing the feed tank a few feet above the press. Easily filtered solids may be separated in a frame 3 inches wide at a pressure of over 100 lbs. per square inch. Frames 1 inch wide are used in general work.

Owing to the facility of forming channels through the press from plate to plate by providing holes in each plate in similar positions, many complicated operations may be performed. The liquid treated may be continuously maintained at a suitable temperature by providing channels in each plate for the circulation of a hot or cold fluid. By the provision of rubber diaphragms and water under high pressure, the cakes may be squeezed before removal from the press. Washing the cakes is simply accomplished by feeding the washing water by means of a special channel behind the filtering cloths of alternate plates, and allowing it to leave the press by a channel connected to the remainder of the plates (Fig. 7). As the washing water rises in the cakes, the imprisoned air is allowed to escape by means of air cocks.

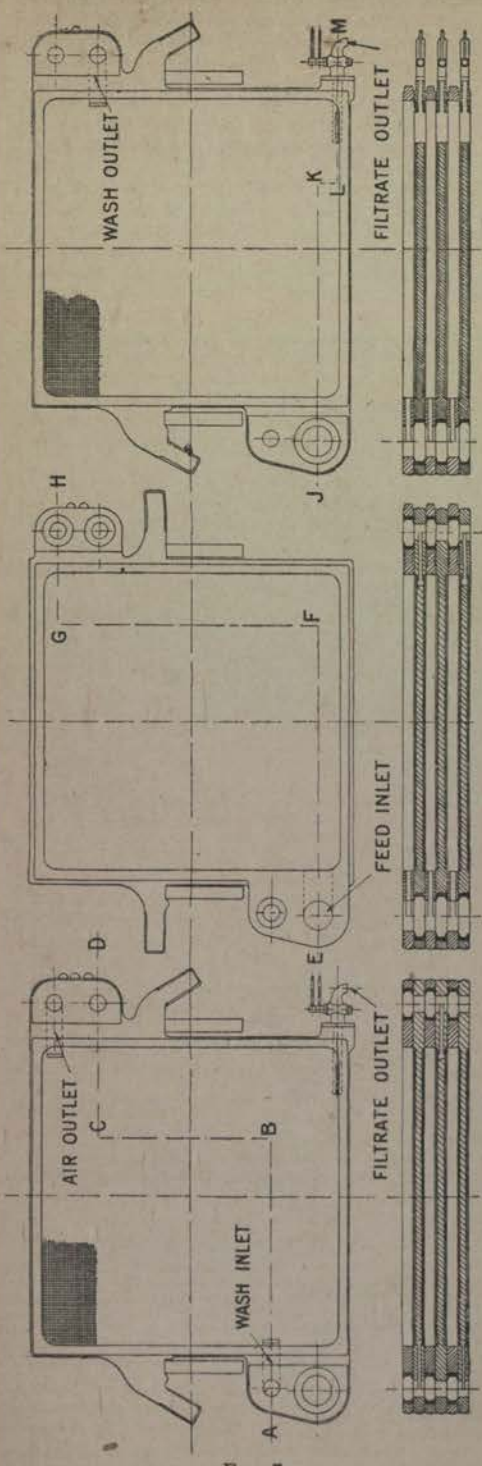


FIG. 7.

The joints between the plates at each of the holes which form a channel through the press, are made by rubber packing rings or by the arrangement of short pieces of rubber pipe so that the internal pressure of the liquid ensures tightness.

Air vessels of ample dimensions should be fitted to pumps feeding filter presses to prevent variations in pressure. Taps are usually provided on each plate for the delivery of the filtrate, so that any plate may be cut out should its effluent become turbid. In starting the filtration, the pressure is applied gradually to build up the filtering layer; with some substances, the filtrate is always turbid for a second or two. In presses where the plates deliver their filtrate into a common channel, small cylindrical filters supported in cages are sometimes provided to stop this action and also, by choking, to automatically stop the delivery of a turbid filtrate through the piercing of any filter cloth. Presses for volatile liquids are usually provided with a cover dipping into an oil or water seal, and connected on occasion with suitable recovery plant.

The materials used as filter cloths are simply well-made strong fabrics—cotton material for most purposes, woollen fabric for dilute acid liquors, and for certain fine work, silk. The filter paper used should be crinkled to admit of its expansion in contact with its supporting fabric. Wire gauze or perforated metal plates are used for some filtrations, a filter bed being first formed by running into the press a pulp of vegetable or mineral fibres. J. W. H.

FINE BLUE, GENTIAN BLUE 6B, SPIRIT BLUE, OPAL BLUE, BLEU DE NUIT, BLEU LUMIÈRE. The hydrochloride, sulphate, or acetate of triphenylrosaniline and triphenylpararosaniline (*v.* TRIPHENYL-METHANE COLOURING MATTERS).

FIRE-CLAY. A refractory clay capable of withstanding a very high temperature without fusion or perceptible softening, and hence largely used for the manufacture of fire-bricks, gas-retorts, crucibles, and glass-house pots. The best fire-clays are obtained from the coal-measures, the most celebrated in this country being that of Stourbridge in Worcestershire. This clay is remarkable for the small amount of contraction which it undergoes when fired, the shrinkage of the unrefined clay being in some cases as low as 1 p.c. (G. Maw). In order to reduce shrinkage, the fire-clay is often mixed with ground potsherds to the extent of about one-third of its weight. The comparative infusibility of fire-clays depends on their high percentage of silica, and on the small proportion of alkalis present. Many highly silicious substances, which are not true clays, have come to be used in the preparation of certain fire-bricks: thus the so-called 'Dinas clay,' from the Vale of Neath in Glamorganshire, largely employed in the copper-smelting furnaces of South Wales, is really a disintegrated sandstone, containing as much as 98 p.c. of silica. Another highly silicious rock is the *ganister*, which forms the seat-stone beneath certain coal-seams in the lower coal-measures of Yorkshire, and is extensively used, when ground and mixed with water, for lining Bessemer converters. The following

analyses represent the composition of certain fire-clays :—

—	I.	II.	III.
Silica . . .	65·10	67·12	68·12
Alumina . .	22·22	21·18	26·69
Ferric oxide .	—	1·85	2·00
Potash . .	0·18	2·02	1·17
Lime. . .	0·14	0·32	1·15
Magnesia . .	0·18	0·84	0·59
Ferrous oxide .	1·92	—	—
Water, combined .	7·10	4·82	0·20
,, hygroscopic	2·18	1·39	—
Organic matter .	0·58	0·90	—
	99·60	100·44	99·92

I. Stourbridge, by C. Tookey. II. Dowlais, by E. Riley. III. Better-bed fire-clay, Bowling, Yorkshire, by J. W. Westmorland. No. I. contained 0·06 p.c. P_2O_5; III. contained 0·87 p.c. TiO_2. Riley has found as much as 1·05 p.c. TiO_2 in a Stourbridge fire-brick.

The fire-clay of Glenboig, Lanarkshire, has been examined by J. W. Gregory and D. P. McDonald (Proc. Roy. Soc. Edin. 1910, 30, 348, 374), who find that the fine-grained clay substance forming the bulk of the material is present as minute rounded granules about 0·001 mm. in diameter; this is amorphous and not crystalline, and is referable to the mineral species halloysite rather than to kaolinite. Embedded in it are abundant grains of quartz, some grains of felspar, and minute crystals of a rhombohedral carbonate referred to sideroplesite (a variety of chalybite).

(For a large series of analyses of British and foreign fire-clays, *v.* Percy's Metallurgy: Fuel, 1875, 87; H. Ries, Clays, their Occurrence, Properties, and Uses, 2nd ed. New York, 1908.)

F. W. R.

FIRE EXTINCTION AND PREVENTION. Combustion, as it exists in ordinary cases of fire, is due to the rapid combination of the burning material with the oxygen of the air at temperatures above the ignition-point, and it may be extinguished either by lowering the temperature of the burning mass below the point necessary for the continuance of the combustion, or by cutting off the access of air, and so depriving the combustion of the oxygen which is essential for its support.

The usual method adopted for extinguishing a fire is to pour on to the blazing material a large volume of water, and this acts partly by rendering heat latent in its evaporation, and so cooling down the burning mass, and partly by the steam generated driving back the air and so giving time for the cooling action to take effect.

The force with which the water is thrown upon the burning body also produces a considerable effect by sweeping the flame from the surface and so extinguishing the burning gaseous products.

Although, in round figures, 1 lb. of well-dried wood on combustion will convert about 5 lbs. of water into steam, yet in the early stages of a fire it is only the surface of the wood that is burning, so that the 5 lbs. of water will have a useful effect over a considerable surface, whilst the steam generated occupies a volume about 1700 times that of the water used.

In the use of water, a certain amount of discretion is necessary, as otherwise undesired results may follow. For instance, in a big warehouse fire, the lower portion soon becomes a mass of red-hot carbonaceous matter, and if water is recklessly played into this, the water is almost instantly turned into steam, which is decomposed in passing through the surrounding red-hot carbon, forming a mixture of hydrogen and carbon monoxide, known as 'water gas.' This gas is inflammable, and by its combustion adds to the general blaze, whilst, if it escapes being ignited, it may collect under ceilings and roofs, where, mixing with air, it forms a highly explosive mixture liable to be ignited by any chance flame or spark.

If, however, the water is directed on to the top of the mass, the carbonaceous matter is cooled downwards, so that the steam evolved does not pass through the glowing carbon, and there is thus the minimum generation of inflammable products.

A fire can also be extinguished by practically smothering it by cutting off the supply of air, and although this is rarely practicable, yet the closing of all doors and windows, by reducing the quantity of air available, checks the combustion.

Water is useless for the extinction of burning oils and spirits, as these, being lighter than water, float on the surface and continue to burn. The best way of treating a fire of this kind is to throw on it sand or earth or anything that will serve to keep the air away, and so cause the flame to die out.

Attempts have been made to employ certain gases which are unable to support combustion, and which can be obtained commercially at a fairly cheap rate, but the advantages of this method are very doubtful, as, unless the whole of the surrounding air can be replaced by an atmosphere of the extinguishing gas, little good results. With a fire well alight in an open space, there is always a strong up-current of hot air and the products of combustion, so that any gas poured on to the fire would be carried upwards out of the area where it would be effective. In certain cases, however, as in confined spaces, this method has its uses. For instance, when a chimney is on fire, the combustion can be stopped by throwing a handful of sulphur on the fire in the grate. The sulphur burns, forming sulphur dioxide, and this being drawn up the chimney cuts off the supply of air from the burning soot and so extinguishes the fire.

The fact that certain gases and salts will extinguish a fire under certain conditions, has led to a variety of apparatus being designed, which are known under the name of chemical extincteurs, and vary in size from the small hand grenade to the horse-drawn or motor-driven chemical fire engine. Amongst the substances that have been brought into requisition for this purpose are such gases as carbon dioxide, hydrochloric acid gas, and ammonia, none of which supports combustion, and salts, like common salt and borax, tungstates and phosphates of the alkali metals, which form a protective coating on the surface of the combustible material.

Extincteurs may be divided into two classes, those in which carbon dioxide is generated rapidly from a charge of some carbonate, such as chalk or sodium carbonate, and an acid in the presence of a large volume of water. The pressure created by the evolution of the carbon dioxide in the containing vessel causes the water to dissolve the gas, and at the same time the pressure drives the water holding the gas in solution through the small hose and nozzle on to the fire. The water, as soon as it is subjected to the ordinary atmospheric pressure and heat, gives up the carbon dioxide, which, together with the steam, drives the air away from the burning material, whilst the cooling effect of the water is aided in the extinction by the salts in solution coating the heated mass.

The substances generally employed for the rapid evolution of the carbon dioxide are sodium carbonate and hydrochloric or sulphuric acid. These chemicals must, of course, be kept separate in the extincteur until the moment when the apparatus is brought into action, and there are several devices for securing this end. In some cases, the acid is contained in a thin glass bottle, which is left unsealed, at the top of the apparatus, whilst the carbonate is dissolved in the water. On turning the containing vessel upside down, the acid runs out of the bottle and mingles with the carbonate solution, causing immediate evolution of the gas. In other forms, the acid is in a sealed bottle, which is broken either by the release of a leaden weight inside the extincteur or by a blow on a plunger from outside. In the large forms of extincteur, the acid is contained in a bottle covered by a lead capsule, which can be pierced when necessary by a lever from outside the apparatus. By multiplying the number of the cylinders, a continuous stream of water charged with carbon dioxide can be obtained, as, whilst one cylinder is in action, the second can be charged ready for use when the first is exhausted.

The second class of extincteur contains solutions of chemicals which coat the combustible materials, and in addition some of them employ chemicals which give off extinctive gases when subjected to the heat of the fire.

One of the most effective of the many solutions that can be used for this purpose is a solution of a mixture of sodium sulphite and ammonium chloride in molecular proportions. When this is thrown upon a hot fire, sulphur dioxide and ammonia are set free and smother the combustion, whilst the remaining combustible gets coated with a glaze of common salt.

For small fires and in the earliest stages of a fire in an enclosed space, extincteurs have proved very useful, but in the open and with a strong conflagration they are perfectly useless. A fire can rapidly and easily be extinguished if it be attacked within a few minutes of its starting, but in the majority of cases the fire originates during the night or when the place is shut up, so that by the time the outbreak is noticed the fire has gained a firm hold. In order to cope with these cases, numerous automatic devices, such as sprinklers, have been brought forward.

The first form of automatic sprinkler was introduced by Major A. Stewart Harrison, who had the idea of fitting the various rooms to be protected with a system of water pipes furnished at the necessary places with nozzles closed by easily fusible metal plugs. Any serious rise in temperature melted the plugs and started the flow of water through the various jets. This device is the basis of many modifications, and although the systems have attained considerable perfection, they have not been adopted to any very great extent in England, a result partly due to the disinclination of owners of property to spend more than they can possibly help in the way of protection, and partly to the fact that the damage caused to the goods by the water is often as great as that due to the fire. In America, however, automatic sprinklers have been widely employed, and many different forms of apparatus are in use.

It is the earlier stages of an outbreak of fire that are the most important from the point of view of ease of extinction, and in order to draw attention as soon as possible to an outbreak of fire in a building, such as a closed warehouse, automatic fire alarms have been devised, which on an undue rise of temperature, complete an electric circuit and ring a bell at a fixed place some distance away, say, at a fire station. The first forms of automatic fire alarm consisted of thermostats, which were sensitive thermometers, into the bore of which were sealed platinum contacts: as the temperature at the seat of the fire rose, the mercury of the thermostat expanded and completed an electric connection, causing a fire alarm to ring. But these were not certain in action, owing to the surfaces of the mercury and platinum becoming dirty and failing to establish contact, so to obviate this trouble, liquids having a cleansing action were introduced above the surface of the mercury to prevent any amalgamation or oxidation and ensure contact.

Another form of thermostat consists of a closed U-tube containing mercury, above the surface of which in each limb a volatile liquid is confined, and one limb is also surrounded by an insulating sleeve. A sudden rise of temperature will cause the liquid to volatilise more rapidly in the exposed limb, and so drive the mercury downwards: this action opens a closed electric circuit and closes a secondary system, which transmits a signal to any required spot. A differential thermostat is also used in connection with a fixed temperature thermostat, which remains stationary until a definite temperature is attained, and then has a long range for a small increase in temperature. After the first warning call has been given, a further rise in temperature gives a fire call.

Some alarms depend for their action upon the unequal expansion of metals, whilst others rely on the difference in rate of expansion between relatively large and small masses of the same metal; but in all cases, the movement brought about by the sudden rise of temperature is made to complete an electric circuit, and thus give warning at some predetermined place.

Although timber, like all organic substances, is combustible and is burnt away when subjected to a high temperature, yet it can be treated in such a way as to render it fireproof, so that, instead of causing it to burn away, intense heat merely chars it. Various substances have been suggested for this purpose, but many of these so-called 'antipyrenes' have proved unsuitable

owing to their injurious effect upon the wood or upon the paints and varnishes used upon it. Common salt was at one time regarded with much favour as a fireproofing material for wood, but its hygroscopic properties ultimately caused its use to be abandoned.

Any substance which is to be used for fireproofing wood must have no deleterious action on the wood or corrode the nails and screws inserted in it, and must also be a stable and non-volatile body, otherwise, although the chemical might do the required work for a short period, if evaporated it would leave the wood as inflammable as before. The compounds, which practical experience has shown to be of use in this direction are ammonium chloride, ammonium phosphate, ammonium sulphate, calcium chloride, magnesium chloride, zinc chloride, zinc sulphate, stannous chloride, alum, borax, boracic acid, and the tungstates.

On a practical scale, the timber is run on a trolley into a large chamber, which is sealed up and then exhausted of air as far as possible. In this way, all the air and moisture are extracted from the cells of the wood, and, after allowing the wood to remain in the vacuum for some time to complete the extraction, the solution of chemicals is run into the chamber, the whole of the contents being then placed under hydraulic pressure, the amount of which is carefully regulated according to the nature of the wood under treatment, as the pressure required by a dense wood would crush and destroy the cells of a lighter timber. A gauge glass on the chamber shows when the right proportion of liquid has been absorbed, when the wood is removed, drained, and dried at a definite temperature. The temperature to which the wood is subjected for drying purposes has a great effect upon the quality of the final product: too high a temperature will cause the wood to be brittle, but if the correct temperature be employed, the wood dries with all its original qualities unimpaired, but with the added property of non-inflammability.

Wood treated in this way, with mixtures of ammonium phosphate and boracic acid, can be worked in just the same way as non-treated wood: it has no injurious effect upon the tools, and will take paints, varnishes, and other decorative material as well as before treatment, whilst nails and screws do not corrode in it.

When wood thus treated is subjected to the action of a flame, charring takes place, as the cellulose of the wood fibre is still left, and under the action of heat is carbonised, but directly the flame is removed the charred mass blackens, and no spreading of the fire takes place. This effect is due to the chemicals used (chiefly ammonium phosphate and boracic acid) being forced into the cells of the wood by the course of treatment adopted, and once there it is practically impossible to remove them. Under the influence of heat, the ammonium phosphate decomposes, giving off ammonia and phosphoric acid, the former of which drives any air out of the wood replacing it by a non-combustible gas, whilst the phosphoric acid together with the boracic acid coat the cell walls with a glaze, which prevents the access of oxygen from the air to carry on further combustion. V. B. L.

FISCHER'S SALT, *Potassium cobaltinitrite.*

FISETIN, FISETOL *v.* YOUNG FUSTIC.

FISH OILS *v.* OILS AND FATS.

FLAGSTONE. A stratified rock which may be split along the planes of bedding into smooth-faced slabs, suitable for use as paving stones. If the stone is too absorbent, or finely laminated, the surface is apt to flake off by the action of frost. As hardness and durability are essential in a flagstone, sandstones are superior to calcareous or argillaceous rocks. The flaggy sandstones are generally micaceous; and their fissility may be partly due to the presence of mica along definite planes. The best English flagstones are derived from the lower coal-measures, the millstone grit, and the Yoredale rocks. Most of the flags used for paving the streets of London are obtained from the Yorkshire coalfield. The Elland flagstone, which is extensively worked, is a fine-grained micaceous sandstone from the lower coal-measures, or ganister series, extending with persistence through the coalfields of Yorkshire, Lancashire, and Derbyshire. In Scotland, the lower old red sandstone yields paving slabs of very large size, the best-known being the dark-grey flagstones of Caithness and the Arbroath pavement of Forfarshire.

F. W. R.

FLAKE WHITE. A variety of white lead (*v.* LEAD). The term is also applied to basic bismuth nitrate.

FLAME.

Incandescence of gases. When solids and liquids are heated beyond a certain temperature by an external source of heat, they become luminous, and the intensity of the light emitted increases very rapidly as the temperature is further increased. There is no reason to suppose that gases would behave differently except in degree, for according to the kinetic molecular theory of matter, light should arise from molecular vibrations occasioned by molecular collisions. It is doubtful, however—whatever may be the case in celestial bodies—whether a gas has ever been brought by artifice into what may be called a state of purely thermal glow. The high transparency of gases to light is correlative to a very low emissivity. Iodine vapour, which is an exceptional gas in its absorptive power, does indeed glow when heated in a glass tube even when the walls are considerably below a red heat, but there is reason to believe that this glow is connected with the dissociation and recombination of the atoms in the iodine molecule (*see* especially Evans, Astrophys. J. 32, 1, 1910).

Attempts to heat colourless gases, such as nitrogen, to the glowing-point, have given negative results.

In almost every case, *a flame is glowing gas*, and in view of the facts just recited we must add the qualification, so far as terrestrial conditions are concerned, that *the glow is the accompaniment of chemical change.* It would be possible to refine upon this definition. A 'flame' of pure hydrogen in dustless air is, according to Stas, invisible, the radiation of short-wave length being wholly in the ultra-violet. Again, the glow observed during the decomposition of acetylene in a hot tube may be due wholly to the particles of liberated carbon and in no degree to anything gaseous. But, speaking generally, the basis of flame is a glowing gas, and the exciting cause chemical

action. This description would include ordinary hot flames and also flames of the kind called phosphorescent, which may be quite cold in the ordinary sense of the word.

If, then, a chemical change takes place, resulting in the production of gas and the liberation of a quantity of latent chemical energy, a flame may make its appearance. Experience shows that this only occurs when the amount of energy liberated is very considerable, in other words, flames are only to be expected during the resolution of highly endothermic compounds, like guncotton, into gaseous constituents, or during the formation of highly exothermic compound gases from their components, as in the case of carbon dioxide from carbon monoxide and oxygen. In phosphorescent flames, such as that of phosphorus, the energy liberated per gram-molecule of product formed is no less considerable.

Flames produced during the decomposition of single endothermic compounds do not call for any detailed consideration, since, apart from their genesis, they do not present many special features of interest. The case of acetylene is interesting, inasmuch as a flame initiated in a column of the gas at one point is not propagated for more than a short distance, unless the gas is under a pressure of about two atmospheres.

Conditions determining flame. The principles underlying flame phenomena are best considered in the ordinary case where the flame is occasioned by combination between two substances, either single substances or mixtures of substances. Such a case as that of coal gas and air is complicated by the fact that both these substances are mixtures, and it is to be remembered that in the intermingling of such mixtures the diffusive power of each component will assert itself and lead, for the moment, to local variations of condition.

In selecting even one of the simplest cases for the purpose of discussing flame phenomenon, it is necessary to premise that there are many factors of which we have at present only an imperfect knowledge, and many doubtless of which we have no conception at all. We may recall, for example, the remarkable discoveries which have been made in recent years concerning the influence of minute quantities of water vapour upon the initiation and intensity of combustion. The mechanism of what was formerly regarded as so simple a chemical phenomenon—the burning of hydrogen—is full of difficulties. H. B. Dixon, discussing this subject very fully (Chem. Soc. Trans. 1910, 97, 661), considers that steam intervenes in the initial action of hydrogen on oxygen at moderate temperatures, but he does not think it necessary for the propagation of a flame once started in the mixture. The mode of action of the steam, which, according to E. W. Morley's calculation, quoted by Bone (British Association Reports, 1910), is present to less than the extent of 4 molecules per 1000 million molecules of dried gas, is at present unintelligible.

Notwithstanding Larmor's conclusion about the infrequency of trimolecular collisions in a gas, and the support thereby given to the theoretical and experimental inference of other workers as to the probability of one molecule of hydrogen uniting initially with one molecule of oxygen, Dixon shows that there are great difficulties in maintaining that hydrogen peroxide is the first product formed in a hydrogen flame.

Similar complications present themselves in nearly every case of combustion. The main phenomena of flame can, however, be usefully discussed without entering into minutiæ of the chemical transactions involved, and this course will be taken in what follows.

Limits of inflammability. In order that a flame of the common type may be produced, it is necessary to have the combining substances mixed in certain proportions, and to heat a portion of the mixture initially to a certain temperature. The proportions within which self-sustaining flame may be incited are called *the limits of inflammability*, and the temperature at which self-sustaining flame is set up is called the *temperature of ignition*.

When a portion of a stationary inflammable mixture is raised to the temperature of ignition, unless the quantity so heated is very minute, a flame travels through the mixture. The flame may, however, be quenched in the neighbourhood of surfaces of high heat conductivity, as, for example, when it enters narrow tubes or impinges upon a fine metallic meshwork. This is the well-known principle which applies in the miner's safety lamp, the flaming fire-damp and air within the lamp being extinguished in contact with the metallic gauze. The rate at which a flame travels through an inflammable mixture depends, apart from the form and material of the enclosure, on the nature of the gases, on their proportion in the mixture, and on the distance traversed. Formerly, the rates of inflammation of gaseous mixtures were supposed to be very moderate. Thus, for hydrogen and oxygen in the proportions of electrolytic gas, Bunsen gave the rate of propagation of flame as 34 metres per second.

The existence of vastly higher rates was first demonstrated by Berthelot, in the discovery of the 'explosive wave,' and as the result of his researches as well as those of Mallard and Le Chatelier and H. B. Dixon, we now know that in many gaseous mixtures the initial slow rate of *inflammation* may be succeeded by a rate of *explosion* or *detonation*, amounting to between 1500 and 3500 metres per second. If mixtures of this kind be ignited at the end of a long tube, the flame first proceeds with a sensibly uniform velocity for a distance of from 0·25 to 1 metre (period of inflammation); then a vibratory movement ensues, which increases in intensity until finally the explosive wave is set up, and the flame proceeds through the rest of the mixture with the high velocity just described.

In connection with flames, we are concerned only with the rates of inflammation, and these are exhibited for a number of mixtures in the diagram (Fig. 1, taken from Bunte) (Ber. 1898, 31, 5).

As will be seen from the diagram, the rate of propagation of flame is not necessarily greatest in mixtures containing the combining gases in the proportions just required for complete combination. The flame in a mixture of 40 p.c. of hydrogen and 60 p.c. of air has a higher rate of propagation than one with 28 or 29 p.c. of hydrogen (the stoichiometric proportions). This apparent anomaly is explained when we

consider that (1) heat evolution per unit volume of the mixture diminishes as we depart from the stoichiometrical proportions; (2) heat conduction from layer to layer increases in rapidity as the proportion of the highly conducting gas (hydrogen) increases, until (3) this accelerating effect of

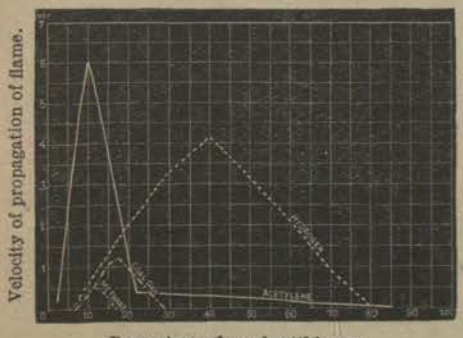


FIG. 1.

the gas in excess is balanced by the diminution of heat evolved per unit volume of the mixture.

Temperature of ignition. The temperature of ignition of gaseous mixtures is, as already stated, for practical purposes, the temperature to which a portion must be heated in order to produce self-sustaining flame. The fact that, as a rule, mixtures are ignited by the sudden application of a very high temperature, such as that of a match flame or an electric spark, led for long to a neglect of the scientific aspect of the subject, and produced the impression, still widely prevalent, that a flame appears necessarily *per saltum*.

In the light of modern experiment and theory, according to which the rate of chemical action varies continuously with increasing or decreasing temperature, we should rather expect flame to appear gradually as the temperature is increased, if it is merely an accompaniment of chemical action. The small proportion of combining molecules in a gaseous mixture at a low temperature might not occasion a perceptible amount of visible short-wave radiation; but as the temperature progressively rose we should expect a glow to appear gradually and to intensify. As the rate of chemical action normally increases very rapidly with increasing temperature, it is unnecessary to suppose that the luminosity would extend over any great range below the temperature of ignition, and, in order to investigate the subject, it is therefore necessary to examine mixtures in that region of temperature. Almost the only case that at once presents itself is that of phosphorus. Phosphorus ignites at about 60°, so that at the ordinary temperature it is within 50° of its temperature of ignition. The fact that its vapour glows at ordinary temperature is the best-known property of phosphorus. The glow diminishes as the temperature is reduced, and disappears at about 7°.

If other combustible substances are examined under corresponding conditions, the vast majority show the same property. All that is necessary is to heat them in admixture with air to a temperature near their igniting-point, when they show all the appearance of 'phosphorescence.'

When phosphorescence begins, the number of molecules combining in a given volume of the gas is small, so that the elevation of temperature of the whole mixture will be small. As the temperature is raised and the phosphorescence intensifies, a greater rate of combination has set in, and the liberation of heat becomes more perceptible.

The foregoing considerations lead to a tolerably precise characterisation of the temperature of ignition. As heat is supplied at an increasing rate to a gaseous mixture, the rate of combination increases, and if the combination itself produces heat, a point will be eventually reached when this heat will be produced with sufficient speed to compensate the loss due to radiation and conduction. The source of external heat may then be withdrawn and the burning will continue. The temperature required to induce this condition is the temperature of ignition. It may be well illustrated by causing the vapour of carbon disulphide to issue from a tube at the mouth of which is a ring of platinum wire that can be gradually heated by an electric current. A phosphorescent flame appears below the temperature of ignition. If the current through the platinum ring be diminished, the flame disappears; if it be raised, the flame increases in intensity until a certain temperature is attained when self-sustaining combustion ensues and accessory heat from the platinum ring is no longer necessary.

The following table of ignition temperatures is taken from a paper by Dixon and Coward (Chem. Soc. Trans. 1909, 95, 514):—

THE IGNITION TEMPERATURES OF GASES.

	Ignition temperature			
	In oxygen		In air	
	Between	Mean	Between	Mean
Hydrogen	580°–590°	585°	580°–590°	585°
Carbon monoxide (moist)	637°–658°	650°	644°–658°	651°
Cyanogen	803°–818°	811°	850°–862°	856°
Ethylene	500°–519°	510°	542°–547°	543°
Acetylene	416°–440°	428°	406°–440°	429°
Hydrogen sulphide	220°–235°	227°	346°–379°	364°
Methane	556°–700°	—	650°–750°	—
Ethane	520°–630°	—	520°–630°	—
Propane	490°–570°	—	—	—
Ammonia	700°–860°	—	—	—

The gases were separately heated to the same temperature and then allowed to meet, and in this way certain difficulties attending earlier methods of determining ignition temperatures were overcome. Another method of determining temperatures of ignition employed by Falk (J. Amer. Chem. Soc. 28, 1517; 29, 1536) and modified by Dixon (Chem. Soc. Trans. 1910, 97, 674), consists in compressing the gaseous mixture under practically adiabatic conditions, and so heating it to the point of inflammation.

Types of flame. A stationary flame with complete combustion may be produced by igniting an inflammable mixture as it issues into a neutral atmosphere, or by allowing one of the combining gases to issue from an orifice into an

atmosphere of the other, and igniting the self-made mixture at the orifice. A third method is to have one gas in excess in the mixture and to allow it to issue into an atmosphere containing the other. All these conditions are found in practice, and they merge into each other. Let us consider the case of a flame of carbon monoxide in air, which lends itself readily to experimental demonstration. (See Fig. 2.)

If undiluted carbon monoxide be sent from a cylindrical tube under a gentle pressure, the flame which is formed is a simple hollow cone of blue light resting upon the orifice of the tube (*a*). If the tube be made of a material of high heat conductivity, there is a perceptible gap of

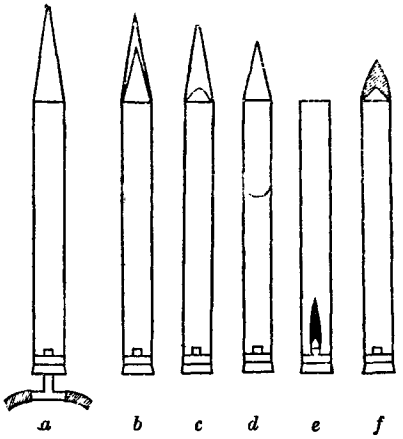


FIG. 2.

extinction between the end of the tube and the superimposed flame. The genesis of the cone is easy to understand. The escaping gas makes its own mixture with air, and so the stream is burned through from the outside as it ascends. The current of gas, moreover, issues with a greater velocity in the axis of the tube than at the sides, where it is impeded by friction against the walls, and the unburned gas in the middle is also heated as it ascends through the burning walls. All these factors promote the conical form of the flame. The form of a carbon monoxide flame issuing from any other kind of orifice can be predicted from similar considerations. Of course, when the velocity of issue increases, the case is complicated by the turbulent motion of the gas.

Let us now consider the effect of adding some air to the carbon monoxide before it issues from the orifice. Air added in this way is often called *primary* air, and the additional air taken from the atmosphere round the orifice to complete the combustion is called *secondary* air. A small quantity of primary air produces a noticeable effect upon the flame. The cone diminishes in height, and seems to have a lining of brighter blue (*b*). With a little more air, the lining is seen to be a second cone within the first, and consequently with a gentler slope. The individuality of this inner cone becomes apparent when the proportion of primary air mixed with the issuing gas is sufficient to bring the mixture well within the limits of 'inflammability' (*c*). The mixture is, indeed, inflaming downwards, but as the rate of propagation does not exceed the upward velocity of the gas stream, the inner cone of flame cannct travel against the gas stream. With more air, however, a greater rate of inflammation ensues, and eventually the inner cone, after becoming more and more squat, enters the tube and travels against the gas stream, first as a flat disc and then as a convex surface with the bulge downwards (*d*). Throughout all these changes, the second or outer cone is maintained at the orifice of the tube by the combustion in the external air of the carbon monoxide remaining in excess of what the primary air suffices to oxidise in the inner cone or disc. It loses in brilliance owing to its dilution with the carbon dioxide and nitrogen which come up from the inner cone. If the primary air supply be further increased, the outer cone will eventually disappear altogether, for a point is reached when the oxidation can be completed by the primary air (*e*). This, however, is not the end point, for an excess of primary air, just like a defect, diminishes the rate of inflammation, and consequently when this rate has been reduced below the velocity of outflow of the gaseous mixture, the single (inner) cone of flame will rise again to the orifice of the tube and remain there. It is to be noted that now the flame consists of only one film of burning gas. The film is still conical, in virtue of the greater axial velocity in the stream of gas, but it has considerable thickness, and its lower boundary is also a conical surface (*f*). There is need of a term to distinguish a flame of gas which is burning continuously throughout the whole or nearly the whole space included by its external surface, from one which is burning in thin films and whose external surface includes chiefly unburned gas. The word 'solid' is sometimes used in this connection, but a 'solid carbon monoxide flame' is obviously a contradiction in terms. Perhaps one might speak of a *volume flame* as distinguished from a *film flame*.

The last stage to be described in the development of the carbon monoxide air flame is reached when the excess of primary air brings the mixture near to the limits of inflammability, or, precisely speaking, when the rate of inflammation of the mixture is reduced below the velocity of the slow-moving part of the ascending gas mixture adjacent to the walls of the tube. The flame then gets detached from the orifice, rises, and disappears.

The various phases are shown diagrammatically in Fig. 2.

In Fig. 2 (*e*) the inner cone, which has retreated, is shown as being arrested at the orifice of the narrow tube through which the mixed gases are led into the wider one. The arrest is due to the fact that the velocity of efflux through the narrow tube exceeds in all cases, for the present example, the velocity of inflammation of the mixture. Mention may here be made of a piece of apparatus used by Smithells (Chem. Soc. Trans. 1892, 61, 204), known as the flame separator, as it depends for its action on the principle just referred to. The separator, Fig. 3, consists of two cylindrical tubes of different diameter, made preferably of fireproof glass, one of which slides within the other through an india-rubber collar. A brass candle adapter attached to the inner tube keeps the inner tube coaxial.

with the outer one. Mixtures of an inflammable gas and air can be admitted through the lower end of the narrow tube by attaching a T-piece, or more simply by attaching it to a Bunsen burner. In all cases, a two-coned flame can be obtained, and if the proportion of the gases is suitably adjusted for a velocity of inflammation intermediate between the upward velocity of the mixture in the wide tube and that in the narrow one, the inner cone will descend in the wide tube and come to rest at the orifice of the narrower one. If the outer cone be now slid down, a two-coned flame rests on the orifice of the narrow tube. The practical value of the appliance depends on the fact that it permits of the aspiration of the interconal gases in a pure state, and in this way it has been of assistance in the study of the progress of combustion in complex gases.

FIG. 3.

Flame temperatures. The principles developed in the discussion of the carbon monoxide air flame are applicable to all flames. We may now apply them in connection with the question of flame temperature.

In speaking of the temperature of flame it is necessary to specify exactly what is meant by the term. Most flames are composed of thin films, and their external surface includes a large quantity of unburned gas. We might speak of the temperature of such a flame as meaning the average thermal state of the burning films and the included gas. This, however, is not the custom. The temperature attainable by the combustion of gas usually means the temperature which would be indicated by a thermometric instrument wholly immersed in the region of combustion. It is obviously very difficult to make such measurements in thin films of flame; in volume flames, produced by burning ready-made mixtures of combustible gas and air it is more practicable to measure the temperature experimentally. Flame temperatures have been measured chiefly (1) by exploding gaseous mixtures and calculating the temperature from the increase of pressure; (2) by means of thermo-couples, especially the platinum platinum-rhodium couple of Le Chatelier; (3) by use of optical pyrometers in cases where the flame contains incandescent solid; (4) by analysis of interconal gases and the application of thermodynamics. The subject, both theoretically and practically, is complicated, and an adequate discussion is impossible within the limits of this article. A 'theoretical temperature' of flame may be calculated from the thermal value of the reaction, and the mass and specific heat of the products. Thus, in the case of hydrogen, taking the heat of formation of a gram-molecule of steam (18 grams) to be 57,560 calories, and the specific heat of steam at constant pressure as 0·4805, we have:

$$\text{Rise of temperature} = \frac{57560}{18 \times 0{\cdot}4805} = 6655°.$$

As a matter of experiment, the temperature of an oxy-hydrogen flame is found to be about 2400° (Féry).

The discrepancy is easily understood, for the calculation involves several assumptions; the action is supposed to be instantaneous, so that no heat is radiated in the process, and the specific heat of steam is supposed to be unaltered at high temperatures. Both these assumptions are in conflict with experimental facts.

Calculated flame temperatures, where air is used, proceed on the assumption that the heat of reaction is distributed among all the products, including the passive nitrogen, so as to bring them to the same temperature. Thus, in the above calculation, we should, if air were used instead of oxygen, add a term for the nitrogen, &c., and so obtain a value of about 2500°.

Temperatures of flames, calculated in this way, for combustion in air, approximate more nearly to the measured temperatures, and the numbers obtained serve at least to give an estimate of the relative temperatures of different flames.

The following table is calculated by Le Chatelier, all the substances being burnt in air:—

C to CO_2	2040°	CH_4	1850°
C to CO	1280°	C_2H_2	2420°
CO	2100°	Producer gas	1350°
H_2	1970°		

To these may be added: combustion of C in air with 5 p.c. unused oxygen in the products, 1950°, ditto with 5 p.c. of CO in the products, 1930°; producer gas with air supply heated to 1000°, 2150°.

How far these calculated figures accord with direct measurements may be illustrated by the following results, given by Féry, who used an optical method:—

MAXIMUM FLAME TEMPERATURES (FÉRY, 1904).

	Deg. C.	Deg. F.
Bunsen burner, gas fully aërated	1871	3400
„ „ insufficient air	1712	3114
Acetylene flame	2548	4618
Alcohol flame	1705	3101
Denayrouze burner, alcohol and air	1862	3384
Do., half each alcohol and petroleum spirit	2053	3727
Hydrogen, free flame in air	1900	3452
Oxy-coal gas blow-pipe flame	2200	3992
Oxy-hydrogen „ „	2420	4388

To these may be added a series of recorded temperatures of the flame of a Bunsen burner using coal gas:

MAXIMUM TEMPERATURE IN THE FLAME OF A BUNSEN BURNER USING COAL GAS.

Date	Deg. C.
1860.—Bunsen and Kirchhoff	2350
1877.—Rosetti	1360
1892.—Rogers	1230
1892.—Lewes	1630
1895.—M'Crae	1725
1896.—Waggener	1770
1899.—Berkenbusch	1830
1902.—White and Traver	1780
1905.—Féry	1871

Only the later numbers are of importance. Féry estimates the temperature of the electric arc to be 3760°, and that of the sun to be 7800°. The temperature of the acetylene-oxygen flame is supposed to be between 3000° and 4000°.

Another aspect of the temperature question presents itself when the practical use of flames is involved. As an example, we may briefly

discuss the use of a coal-gas air flame for heating a Welsbach mantle. The object is, of course, to get the maximum flux of light from the consumption of a fixed amount of coal gas, in other words, we seek to raise the maximum mantle surface to the maximum temperature. A primary consideration is, that as the temperature is raised the intensity of light emitted increases in a much more rapid ratio. The total energy radiation of an ideally 'black body' increases as the fourth power of the absolute temperature, and of this radiation the proportion which is visible also increases in a rapid ratio. This is especially the case with the Welsbach mantle which has a selective radiating power for short wave lengths. Even a small reduction in temperature must therefore be accompanied by a loss of intrinsic brilliance.

Again, having regard to the shape of a mantle, to its inevitable irregularities, original or acquired, and to the unsteadiness of a flame, it is evident that a high temperature can only be attained when it is suspended in a tolerably thick stratum of flame, although the mantle has doubtless a steadying and localising effect on the flame.

Reverting to the discussion of the carbon monoxide air flame we may easily apply the conclusions to the case of a Bunsen burner, using coal gas and air. This burner, as used in its ordinary form, draws in through the air ports at the base (by the injector action of the coal gas escaping from the nipple) from 2 to 2½ times its volume of air, about half the amount required for complete combustion. This air effects a partial oxidation of the coal gas, and yields an inner cone of flame; the oxidation is completed when the products from the inner cone mingle with the external air, an outer cone being formed. A Bunsen or 'atmospheric' burner thus gives a double flame. If the two cones be separated by a considerable interval in the flame separator, it is easy to show that the temperature reigning in the inner cone exceeds that in the outer cone, but if the two cones are close together, the reverse is the case. The explanation is to be found in the fact that when the two cones are near, the gases coming to the outer cone have still a high temperature from the act of their formation, and their temperature is to be added to the rise occasioned by the completion of their combustion, in the outer cone. From this it might appear that the best disposition of a mantle in the flame would be that in which it occupies the surface of the outer cone. But it is to be remembered that the mantle deforms the cone by altering the currents of gas and air, and, besides, the outer surface of the mantle will lose heat very rapidly if it is at the confines of the flame. We should rather suppose, therefore, that it would be better to submerge the mantle in the flame to some extent, and if this is done and if at the same time by the use of a glass chimney we cause a more rapid flux of air round the flame to quicken the combustion in the outer cone, we get the conditions which, as a matter of fact, have been found most effective for heating a mantle with the original type of Bunsen burner.

The great gain to be secured by raising the temperature of the mantle soon led to modifications of the original Bunsen burner, whereby it was sought to introduce a larger proportion of primary air. A large number of devices have been used, of which the two most important relate to the form of the burner tube and to the construction of the burner head.

In the well-known Kern burner, the tube is formed on the Venturi principle, and has internally the form of a hyperbolic spindle A. This secures an intake of primary air which is practically sufficient for complete combustion. The mixing of air and gas and the stability of the flame are secured by an expanded burner head, capped by a serrated disc B, through the teeth of which the gas mixture issues in narrow streams. These streams coalesce and produce a conical sheet of flame of uniform character and sensible thickness. The flame, in fact, is of the blowpipe type (Fig. 4A).

The Méker burner is constructed on much the same principle, but the gas mixture passes from the expanded burner head through a deep metal grid. The flame is therefore a cone of gas burning through and through. It will be seen that the Kern flame is designed specially for heating a mantle, whilst the Méker flame is designed to confine the combustion to the smallest attainable volume and to provide a very compact hot flame for general laboratory or furnace use (Fig. 4B).

Increased in-draught of air can also be secured by the use of chimneys. If the gas or

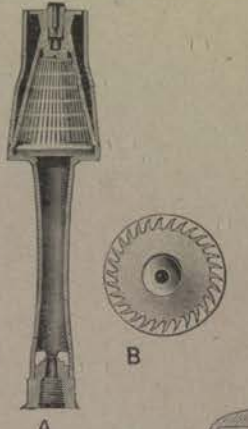


FIG. 4A.

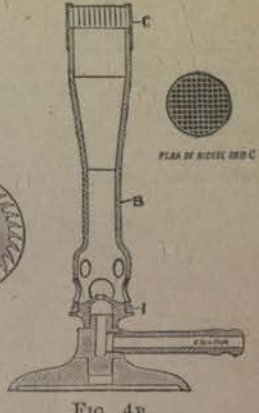


FIG. 4B.

air or both are put under extra pressure and so delivered with high velocity, volume flames may be obtained, which, unlike that of a Méker burner, have their base blown up into a cone, so that the flame appears to be two-coned. This really constitutes a blowpipe flame.

The inversion of a Bunsen flame modifies its form in such a way as to make it more efficient for heating a mantle. The outer film of flame becomes shorter, thicker, and more globular, and as the products of combustion necessarily drift back past the flame, there is a certain recuperation of heat.

The efficiency of various flames for giving lights may be gathered from the following table of illuminating value per cubic foot of gas consumed. The numbers are, of course, only approximate, but they give an idea of the temperatures to which the mantle is raised.

The fact that in all cases the same chemical action is taking place shows how misleading the term 'flame temperature' may be unless the precise character and use of the flame are specified:—

Form of burner	*Candle-power per cubic foot consumed*
Ordinary batswing	2·5
Argand	3·25
Wenham (regenerative)	8–9
Upright, with mantle	20–40 (according to pressure)
Inverted ,,	20–70 ,, ,,

The hottest flame that is in practical use is that of the acetylene-oxygen blowpipe. In this case, we have not only the heat of oxidation of the carbon and hydrogen involved, but also the positive heat of decomposition of the molecule of acetylene. The acetylene-oxygen flame can be used for welding iron and also for perforating steel. (*V.* ACETYLENE; OXYGEN.)

The chemical changes taking place in flames. In the foregoing part of this article, attention has been drawn to general principles which are applicable to flames as a whole, without particular regard to the detailed features of structure or the stages of chemical decomposition. Before discussing any flame in particular, we may adduce one or two further general considerations with regard to chemical changes in flame. It has been assumed, for the sake of simplicity, that in the flames of hydrogen and carbon monoxide the chemical change takes place in one simple step. When we come to other combustibles, it is obvious that such assumptions may be still less warrantable. If, for example, we are dealing with a combustible element which is capable of affording two oxides, we may have the oxidation in the flame taking place in two stages, each stage producing a distinctive feature in the flame. Or, if we have a combustible consisting of two or more oxidisable elements, the oxidation might conceivably take place selectively. Again, in a compound combustible, it is possible that the oxygen may, in the first instance, add itself to the molecule of combustible, producing a complex substance which is ultimately resolved. Lastly, it is possible that the heating effect of the burning envelope in a flame may produce a purely thermal chemical effect on some of the enclosed unburned gas.

Only in a few cases has the progressive combustion in flames been studied fully. In the case of a cyanogen-air flame, it has been shown (Smithells and Dent, Chem. Soc. Trans. 1894, 65, 603) that the inner crimson film of the flame marks the combustion of the gas to carbon monoxide, whilst in the blue fringe of the flame the oxidation is completed by the combustion of the carbon monoxide.

The case of hydrocarbon flames is naturally the one of most interest. The earliest investigations of the progress of combustion, made by Hilgard, Landolt, and Blochmann, in Bunsen's laboratory, dealt with the flames of the complex combustibles, wax, vegetable oils, coal gas, and consequently the results were not very easy to interpret. In more recent times, the combustion of single hydrocarbons has been carefully examined.

The flame of a hydrogen-carbon compound, or of a mixture containing some quantity of hydrocarbons, shows three distinct parts when produced in the ordinary way. Of these, the most conspicuous is the bright yellow patch from which the chief flux of light takes place. The lower part of the flame is surrounded by a bright-blue sheath or 'calyx,' which thins off and ends where it overlaps the lower part of the yellow region. In addition to this, the whole flame is surrounded by a complete mantle of dimly burning gas. The flame is hollow, that is to say, it is filled with unburnt gas, and even the bright-yellow region is an extremely thin conical sheet. A diagrammatic section of a normal hydrocarbon flame is given in Fig. 5.

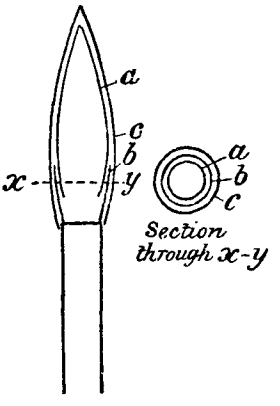


FIG. 5.

The relative development of the different parts is, of course, different in different flames. It depends on many factors, the chief of which are the richness of the gas in carbon, the character of the orifice, and the rate at which the gas issues. The flame of acetylene, suitably developed by allowing the gas to issue in such a way that it is spread out into a thin sheet, shows a very large yellowish-white luminous region, in the glare of which the other parts of the flame are indistinguishable. On the other hand, an alcohol flame exhibits scarcely any yellow luminosity.

If we take the flame of a hydrocarbon burning in an ordinary Bunsen burner with the air ports closed, and then gradually open the ports, we can see how the luminous flame passes into the 'atmospheric' type, and convince ourselves that the blue calyx and the mantle of the luminous flame represent respectively the inner and outer cones of the Bunsen flame. Turning a luminous flame low to the point where only a blue button of light remains at the burner tip, enables us to see a like transition.

The changes experienced by hydrocarbons when burning in a Bunsen burner were investigated by Smithells and Ingle by the use of the cone-separating apparatus already described (Chem. Soc. Trans. 1892, 61, 209), and the analyses of the interconal gases (after cooling) showed in all cases that a partial combustion had taken place, leaving very little of the original hydrocarbon unoxidised. The products of partial oxidation were carbon monoxide, carbon dioxide, hydrogen, and water vapour, accompanied, of course, by the nitrogen of the 'primary' air supply. The following are some of the analytical results:—

Gas employed.	C_2H_4	CH_4	C_2H_6	Coal gas
CO_2 . .	3·6	6·8	13·1	4·2
H_2O . .	9·5	17·6	7·7	16·0
CO . .	15·6	4·5	5·0	8·8
Hydrocarbon	1·3	—	0·6	—
H_2 . .	9·4	3·9	0·6	9·3
N_2 . .	60·6	67·2	73·1	62·0

These analyses refer to the cooled gases, but experiments (unpublished), made by a modification of Deville's method to entrap and preserve the gases as they exist at the high temperature, have not given any ground for doubting that the figures given in the table represent essentially the changes that occur in the inner cone. Independent experiments by Haber and Richardt (Zeitsch. anorg. Chem. 1904, 38, 5) bear out this conclusion.

We may say, therefore, that the inner cone of a Bunsen flame (and the corresponding blue calyx of a luminous flame) marks the region of a partial oxidation in which no carbon, but some hydrogen, remains unoxidised. In the outer cone (and the corresponding mantle of a luminous flame), the carbon monoxide and hydrogen coming from the inner cone (or calyx) find, and are burning with, the air necessary to complete their oxidation.

The experimental results just described stood in direct opposition to a view which, notwithstanding repeated contradictory evidence, had prevailed for three quarters of a century, namely, that in the combustion of a hydrocarbon with a deficiency of air, the hydrogen was preferentially or selectively oxidised, and the carbon set free. It might now be said that there is a preferential or selective combustion of the carbon. The use of these expressions has, however, been objected to, and need not be insisted upon. The objection arises chiefly from a consideration of the results obtained in recent years by a long and careful series of studies made by W. A. Bone and his collaborators, on the progressive oxidation of hydrocarbons from a temperature of 250° upwards. The results of these experiments are summarised in a valuable Report on Gaseous Combustion, drawn up by Professor Bone for the British Association (*see* B. A. Report, Sheffield, 1910), and in this report references to the original papers will be found. According to Bone, 'the attack of the oxygen upon the hydrocarbon may be supposed to involve a series of successive "hydroxylations," the hydroxylated molecules either breaking down or undergoing further oxidation, according to their relative stabilities and affinities for oxygen at the particular temperature.' The following is the scheme for ethane :—

(*a*) Slow Combustion at 300°–400°.

$$\underset{\text{Ethane.}}{CH_3{\cdot}CH_3} \rightarrow \underset{\text{Ethyl alcohol.}}{CH_3{\cdot}CH_2OH} \rightarrow CH_3{\cdot}CH(OH)_2$$

$$H_2O + \underset{\text{Acetaldehyde.}}{CH_3{\cdot}CHO} \rightarrow$$

$$\rightarrow CO + H_2O + \underset{\text{Formaldehyde.}}{H{\cdot}CHO} \rightarrow \underset{\text{Formic acid.}}{H{\cdot}COOH} \rightarrow \underset{\text{Carbonic acid.}}{CO(OH)_2}$$

$$\overbrace{CO + H_2O} \quad \overbrace{CO_2 + H_2O}$$

(*b*) Explosive Combustion.

$$\overset{0}{CH_3{\cdot}CH_3} \rightarrow \overset{1}{CH_3CH_2OH} \rightarrow \overset{2}{CH_3{\cdot}CH(OH)_2}$$

$$\overbrace{\begin{Bmatrix} C_2H_4 + H_2O \\ 2C + 2H_2 + H_2O \end{Bmatrix}} \quad \overbrace{\begin{matrix} CH_3{\cdot}CHO + H_2O \\ \overbrace{\begin{matrix} CH_4 + CO \\ C + 2H_2 + CO \end{matrix}} \end{matrix}}$$

The experimental basis of these schemes lies in the actual isolation of the various members of the series of transition substances implicated.

Space allows of only one further reference to these investigations. Bone considers that one of the most significant features 'has been the proof afforded of the relatively much greater affinity of hydrocarbons as compared with that of either hydrogen or carbon monoxide, for oxygen at the high temperature of flames.' Thus in the explosion of a mixture corresponding to $C_2H_4 + H_2 + O_2$ there is practically no formation of steam.

Luminosity of hydrocarbon flames. In the preceding paragraphs, the chemistry of the combustion of hydrocarbons in the Bunsen flame and in the blue parts of luminous flames has been explained in its general features. It remains to explain the development of the yellow luminous region of hydrocarbon flames. As is well known, the first explanation was given by Humphry Davy, in 1816, among many other observations upon flame still well worthy of attention. Davy attributed the luminosity to the deposition of solid charcoal, which he said 'might be owing to a decomposition of a part of the gas towards the interior of the flame where the air was in smallest quantity.' The ambiguity of this explanation and its supposed implication of a selective combustion of the hydrogen, have already been alluded to. Starting from this 'solid particle' explanation of the light of a hydrocarbon flame, Davy was led to consider that all flames of high luminosity contained solid particles. He knew that the phosphoric oxide was gasefied at the temperature of a phosphorus flame, yet he believed that, in the flame itself, solid particles of the substance were produced, and were conserved by the elastic force of the flame producing a kind of compression.

Davy's explanation remained unassailed until 1867, when E. Frankland made an important series of researches on the luminosity of flames. He concluded :

(1) That bright flames exist which do not contain solid particles.

(2) That the luminosity of flames depends mainly on the density of the substances contained in them.

(3) That feebly luminous flames may be made bright by compressing the burning gases.

(4) That the luminosity of ordinary hydrocarbon flames, such as that of coal gas, is not due, in any important degree, to solid particles of carbon, but almost entirely to the glow of dense hydrocarbon vapours.

Frankland attributed luminosity to the density of the hot gases in the flame, whether this density were due to high molecular weight or to compression. So far as hydrocarbon flames are concerned, Frankland's views were soon submitted to destructive criticism, especially by Heumann.

A crucial experiment indicating the presence of solid particles in flame, first proposed by Soret and subsequently by Burch and by Stokes, consists in focussing the image of the sun on to the flame and examining the scattered light with a Nicol prism. That test, applied to a hydrocarbon flame, gives a positive result, and the presence of solid particles in such flames is no longer disputed.

It is true that the black soot deposited on cold objects introduced into luminous hydrocarbon flames is by no means pure carbon, but

this is to be expected when we remember that any condensible hydrocarbon in the flame would be deposited along with particles of pure carbon, if such were, in fact, present.

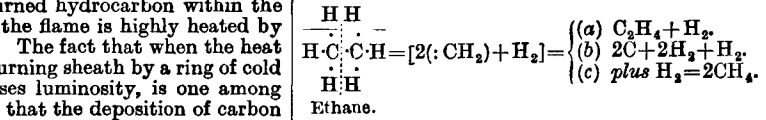
It may now be taken as agreed that the luminosity of hydrocarbon flames is due to the separation of solid particles of carbon. The process by which the carbon becomes separated in the flame has been the subject of much experiment and discussion. Is it involved directly in the oxidation that is taking place, or is it merely a thermal effect—and in either case, what are the stages of the process? It is impossible here to give more than a brief summary of the views that have been held. In the first place, it may be said that the old, simple, and plausible explanation of a preferential oxidation of hydrogen is untenable for reasons already given. In the next it may be affirmed that, generally speaking, hydrocarbons, subjected to a high temperature, deposit solid carbon. It would appear, therefore, that the separation of carbon in a flame might be adequately explained by the fact that the unburned hydrocarbon within the burning sheath of the flame is highly heated by the burning parts. The fact that when the heat is tapped for the burning sheath by a ring of cold wire, the flame loses luminosity, is one among several indications that the deposition of carbon is a secondary and a thermal effect of the combustion. At the same time, the experiments of Bone would lead us to be cautious in denying that in some cases the chemical processes might contribute to the separation of carbon.

Taking it for granted that the decomposition of the hydrocarbon is purely thermal, we may next consider the stages that are passed through. This raises the whole question of the thermal decomposition of hydrocarbons, a subject of great experimental difficulty, on which really satisfactory results have only been obtained over a small range of substances (*see* Bone and Coward, Chem. Soc. Trans. 1908, 98, 1197).

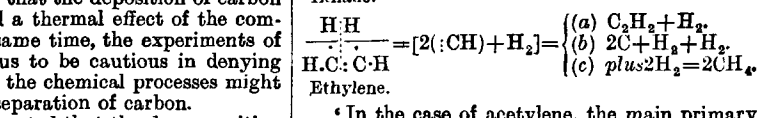
The view that ethylene, on heating, undergoes the simple change $C_2H_4=C+CH_4$, which long served to explain the luminosity of flames, is no longer tenable. The doctrine of Berthelot, according to which the molecules of hydrocarbons, on heating, undergo progressive coalescence with elimination of hydrogen until in the end a molecule is left containing a negligible proportion of hydrogen, is likewise contradicted by modern experiments. The hypothesis of V. B. Lewes (Proc. Roy. Soc. 1895, 57, 450), that the formation of acetylene and its subsequent decomposition are the essential cause of luminosity in hydrocarbon flames, is regarded by those who have concerned themselves with the subject as based on wholly insufficient evidence.

Bone and Coward have been led to the conclusion that the thermal decomposition of hydrocarbons is too complex a phenomenon to be represented by ordinary chemical equations. Dealing with methane, ethane, ethylene, and acetylene, they observe first of all that whilst at a high temperature methane, the most stable of the hydrocarbons, is resolved directly into carbon and hydrogen, this only takes place in contact with solid surfaces, whilst with the three other gases decomposition takes place throughout their bulk.

They say: 'In the cases of ethane and ethylene, it may be supposed that the *primary* effect of high temperature *is* to cause an elimination of hydrogen with a simultaneous loosening or dissolution of the bond between the carbon atoms, giving rise to (in the event of dissolution) residues such as $:CH_2$ and $:CH$. These residues, which can only have a very fugitive separate existence, may subsequently either (*a*) form $H_2C:CH_2$ and $HC\vdots CH$, as the result of encounters with other similar residues, or (*b*) break down directly into carbon and hydrogen, or (*c*) be directly "hydrogenised" to methane in an atmosphere already rich in hydrogen. These three possibilities may all be realised simultaneously in the same decomposing gas in proportions dependent on the temperature, pressure, and amount of hydrogen present. The whole process may be represented by the following scheme, the dotted line indicating the tendency to dissolve the bond between the carbon atoms which becomes actually effective at higher temperatures :—

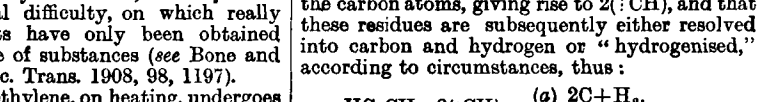


Ethane.



Ethylene.

'In the case of acetylene, the main primary change may be either one of polymerisation or of dissolution, according to the temperature, and, if the latter, it may be supposed that the molecule breaks down across the triple bond between the carbon atoms, giving rise to $2(:CH)$, and that these residues are subsequently either resolved into carbon and hydrogen or "hydrogenised," according to circumstances, thus:



Polymerisation.

'Incidentally, it may be observed that the rates of decomposition of these hydrocarbons are very much slower than their rates of combustion, and that therefore in the propagation of a flame through a homogeneous mixture of a hydrocarbon and oxygen, oxidation will probably take precedence of all other chemical phenomena.'

The chemistry of a hydrocarbon flame has now been given as completely as present knowledge and the limits of space allow.

The art of getting the maximum of light from a hydrocarbon solely by its own combustion may be deduced and stated briefly as follows: The gas must be so burned as to liberate within the burning walls of its flame the maximum amount of solid carbon that can be heated to a high temperature and be wholly oxidised as well. Spreading out the gas stream increases the relative proportion of hot non-luminous burning walls, and diminishes the central zone of unburned gas from which the solid carbon has to be derived. It is on the right adjustment of these two elements of a flame for the particular gas in use, that the construction of a suitable

burner depends, and it is obvious that the best result can only be maintained when the composition of the gas and air, the pressure, and temperature are kept constant. Of course, the question is complicated when we introduce the factors of chimneys and heat-regenerating devices.

It may be convenient here to revert to the question of obtaining the highest temperature from the combustion of a fixed amount of a hydrocarbon. Fig. 6 is reproduced from

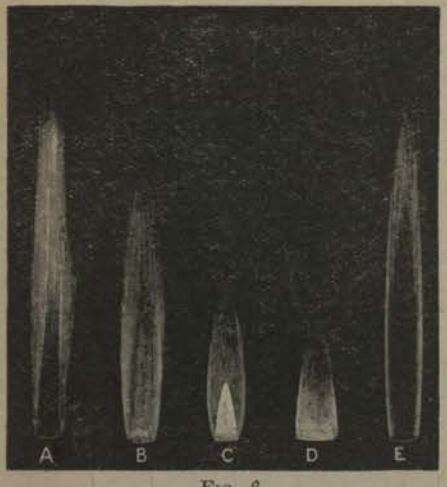


FIG. 6.

photographs of five gas-flames, where the rate of gas flow was constant. In the first flame, A, we have the gas burning (with some smoke) without any 'primary' air[1]; in the second, we have just sufficient primary air to cause delumination; in the third, we have as much air as possible without producing instability; in the fourth, a Méker burner is used; in the fifth, we have the gas mixed, before issuing from the burner, with enough carbon dioxide to produce delumination. Speaking of each flame as a whole, we may say that the hotness is greater in proportion as the surface is less. In the carbon dioxide-fed flame, neutral molecules of that gas are wedged in between those of the combustible gas, and the mixture has to wander far before it gets mixed with enough oxygen to sustain combustion. When it acquires this oxygen, there is round each burning molecule not only the inert nitrogen of the air but the equally inert carbon dioxide. The flame is a thin, single, hollow sheet, and the temperature is quite insufficient to decompose any of the hydrocarbons within. It has the non-luminous appearance of a Bunsen flame, but it is, of course, absolutely the opposite of that in its genesis, for it represents delayed and diluted instead of quickened and concentrated combustion.

The limits of space have rendered necessary the omission of many matters relating to the chemistry and physics of flame. The exact molecular and sub-molecular mechanism by which the luminosity of wholly gaseous flames is regulated, is a subject of great interest. It is now generally believed to be associated with electronic transactions. Some discussion of the subject is to be found in the British Association's Report, Leicester, 1907 (Smithells' address to Section B). A. SM.

FLASH LIGHTS. A term usually applied to combustible mixtures which burn with a brilliant light and more or less instantaneous flash, and which are employed specially for photographic purposes. Slower-burning mixtures, which also yield a bright light on combustion, such as are used for signalling purposes, are known as *flares* (*see* BENGAL LIGHTS; INDIAN FIRE; PYROTECHNY).

For photographic purposes, it is essential that the flash light should be (1) sufficiently brilliant, (2) of the desired rapidity, and (3) specially rich in actinic light. Of all the known available materials which, on combustion, yield a bright and highly actinic light, the metal magnesium stands pre-eminent; and the earliest and simplest methods of employing this substance consisted in projecting a definite quantity of the finely powdered metal into the flame of a spirit lamp.

Various contrivances have been devised for this purpose: one simple plan is to place the charge of magnesium powder in the bowl of a clay tobacco pipe to the mouthpiece of which is attached a rubber ball. A loose plug of tow or cotton wool, wetted with methylated spirit, is then lightly inserted into the mouth of the bowl: the spirit is ignited and, on suddenly squeezing the ball, the magnesium is thrown into the flame.

The next development consists in mixing the powdered magnesium with some highly oxygenated salt, such as potassium chlorate, in such proportion that the mixture, when placed in a small heap upon a metal tray, could be ignited by a match or taper, and would burn with much the same rapidity as a similar small heap of gunpowder. The danger inherent in such mixtures was found to be greatly reduced by substituting barium chlorate for the potassium salt; and more recently, since potassium perchlorate has become a common commercial article, this compound is more usually employed in preference to the chlorates.

Mixtures of magnesium with certain nitrates of the so-called rare earths have been made the subject of patents. One such consists of:

Magnesium powder 10 parts
Thorium nitrate 10 ,,

and a rather less quick mixture contains:

Magnesium powder 10 parts
Zirconium nitrate 5 ,,

One of the chief drawbacks to magnesium flash powders is the volume of white smoke of magnesium oxide which is produced on their combustion, and many efforts have been made to obviate this nuisance. Some of these are purely mechanical contrivances for withdrawing the smoke, but others are attempts to produce mixtures which shall emit little or no smoke.

The two following mixtures claim to yield smokeless magnesium flash powders:—

(1) Powdered magnesium, barium peroxide, and collodion. The charge of powder is blown by means of a pneumatic pump into a small iron crucible heated by a Bunsen burner.

(2) 1 part of magnesium powder mixed with

[1] The unsteadiness of this flame makes it appear somewhat too large in a photograph.

1 part of either silicic acid ('infusorial earth'), barium sulphate, anhydrous calcium sulphate, anhydrous magnesium sulphate ('kieserite'), or boric acid.

It is further claimed for this mixture that if loaded into a cylindrical case with a constricted opening, a non-instantaneous or 'time' flash may be obtained.

At the present time, since the pyrotechnic possibilities of finely powdered aluminium have become known, in most flash powders the magnesium is usually more or less replaced by aluminium, in some cases even wholly replaced; one such mixture consists of:

Aluminium powder	40 parts
Potassium perchlorate	60 „

It is usual, however, to retain some of the magnesium in order to ensure the necessary high actinic quality of the light emitted. Thus a typical mixture consists of:

Powdered magnesium	100 parts
Powdered aluminium	50 „
Ferric oxide	30 „
Copper carbonate	30 „
Magnesium sulphate (dry)	5 „

The following mixtures claim to be non-explosive and almost smokeless:—

(1) Powdered magnesium and aluminium (the quantity of aluminium usually varying from ¼ to ½ the amount of magnesium), mixed with peroxides of calcium, magnesium, or manganese.

(2) Powdered magnesium and aluminium mixed with perboric acid or tungstic acid or their salts.

(3) Powdered magnesium and aluminium, with sulphate of cerium or thorium, or an alum. For example:

Powdered magnesium	8 parts
Powdered aluminium	2 „
Finely powdered, dry chrome alum	10 „

Many mixtures containing aluminium as an ingredient are rendered more rapid in their combustion by the addition of silica, while their rate of combustion may be retarded by the introduction of regulated quantities of carbonates of alkalis or alkaline earths or oxides of the latter. Thus the above mixture may be converted into a slow-burning 'time' mixture by the addition of 2 parts of an alkaline earth oxide or carbonate.

Flash powders are now frequently loaded into small cases or cartridges; ignition of the mixture being effected sometimes by an electric arrangement and sometimes by means of an inserted strip of magnesium ribbon. In the former case, the two electric wires are fixed into the cartridge, with either a short spark-gap or joined by a fine incandescing wire.

One of the many patented cartridges has a case which is itself inflammable. It consists of a short celluloid cylinder closed at the bottom with a cork saturated with collodion, and at the top with a disc of cork saturated with an emulsion of magnesium. Through this, there is inserted a short strip of magnesium ribbon which, on ignition, communicates its combustion to the charge.

A number of contrivances have been devised for producing a rapid succession of flash lights for purposes of cinematograph photography. These consist essentially of mechanical devices for the intermittent feeding of metallic magnesium against the two metal terminals of an electric circuit. G. S. N.

FLAVANILINE *v.* QUINOLINE.

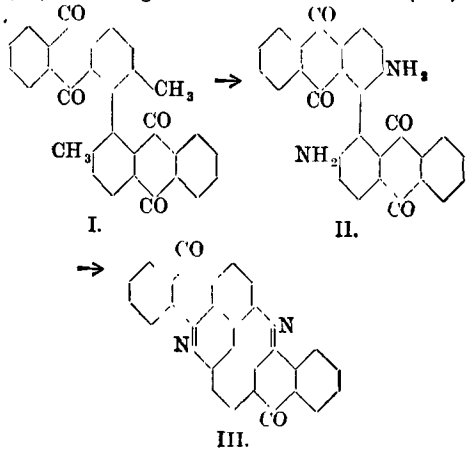
FLAVANTHRENE $C_{28}H_{12}O_2N_2$. An anthracene dyestuff discovered by R. Bohn of the Badische Anilin- und Sodafabrik, by melting β-aminoanthraquinone with caustic potash. Has a large application for unmordanted vegetable fibres, which assume a deep-blue colour in the reduced vat, changing after a few minutes' exposure in the air to a permanent yellow. The colour is very fast, except when subjected to powerful rays of sunlight, which cause it to assume a temporary green shade.

Prepared technically from 2-aminoanthraquinone and potassium hydroxide at 350° (D. R. P. 133086), with aluminium chloride (D. R. P. 136015); with antimony pentachloride in boiling nitrobenzene (D. R. P. 138119); by oxidising with chromic acid or other acid oxidising agents (D. R. PP. 139633 and 141355); in the last-named case, it is accompanied by indanthrene, to which it is closely related (*v.* INDANTHRENE).

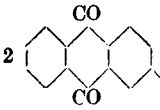
Flavanthrene is a weak base, sparingly soluble in high-boiling solvents, and very stable towards heat; it exists in glistening, brown-yellow needles. It is applied to the fibre after reduction with alkaline hyposulphites, forming a deep-blue vat (D. R. PP. 139634, 139835, 140573, 142963).

The constitution of flavanthrene has been determined by R. Scholl and his co-workers (Ber. 1907, 40, 1691) in the following manner:—

1-amino-2-methylanthraquinone was converted by the diazo- reaction into 1-iodo-2-methylanthraquinone, $C_{15}H_9O_2I$, which passes by means of Ullmann's copper method (Annalen, 1904, 332, 38) at 270° into 2:2'-dimethyl-1-dianthraquinonyl (I.). This substance has also been prepared from the diazonium sulphate of the methylanthraquinone by means of copper powder and acetic anhydride (Knoevenagel, Ber. 28, 2048), and, when oxidised with chromic acid, yields the corresponding dicarboxylic acid $C_{30}H_{14}O_8$. The acid-amide derivative was readily obtained from this in the ordinary way, and the application of Hofmann's reaction with bromine and potash converts it into the amine (II.) and a stage further into flavanthrene (III.).



Flavanthrene must therefore have the annexed constitution III., and in obtaining it from 2-aminoanthraquinone in the process of manufacture, two molecules must unite with loss of two molecules of water and two atoms of hydrogen, according to the scheme:



$= C_{28}H_{12}O_2N_2 + 2H_2O + H_2.$
Flavanthrene.

As the application of this dyestuff to the fibre depends upon its behaviour towards reducing agents in the vat, just as in the analogous case of indigo, careful investigations have been carried out by R. Scholl and his assistants (Ber. 1908, 41, 2304), under a variety of conditions, which show that the reduction products of flavanthrene consist of some seven definite compounds:

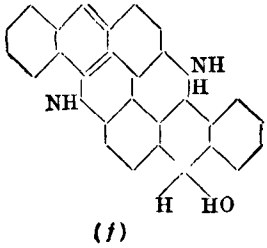
(*a*) *Dihydroflavanthrene hydrate*, obtained by reducing flavanthrene with alkaline sodium hyposulphite in an atmosphere of hydrogen. On cooling, bronze-coloured needles of the disodium salt of this hydrate crystallise out, and by acidifying with acetic acid, the free dihydroflavanthrene hydrate is isolated as bluish-green coppery crystals, which remain stable at the ordinary temperature, but readily oxidise to flavanthrene at 100° or when moist.

(*b*) *Dihydroflavanthrene* is obtained from the above by dehydration at 150°–170° in a stream of carbon dioxide; it consists of a green powder which is more stable than the hydrate. It may also be prepared by reducing flavanthrene with hydriodic acid and red phosphorus at 125°. Although flavanthrene itself is only a weak base, this dihydro derivative readily forms salts with mineral acids; dihydroflavanthrene hydrochloride probably contains the acid united to a N- atom. The *o*-benzoyl derivative melts at 220°.

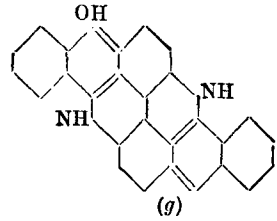
(*c*) *α-Tetrahydroflavanthrene hydrate* is isolated in the form of its sodium salt when flavanthrene is reduced with zinc-dust and caustic soda. On acidifying, (*a*) and (*f*) are formed.

(*d*) *Flavanthrine hydrate*, prepared by reducing flavanthrene with hydriodic acid and red phosphorus at 210°, is a greenish-brown powder, losing water at 240° with formation of *flavanthrine*, which consists of large brown needles with a metallic lustre, m.p. 39°. It is readily oxidised to flavanthrene.

(*e*) *α-hexahydroflavanthrene*, and (*g*) *Flavanthrinol*, are both formed by energetic reduction of flavanthrene with zinc-dust and caustic soda.



(*f*)



(*g*)

(*f*) is a stable blue-black powder which loses water at 160°; dissolves in alcohol to a bluish red solution with a brilliant scarlet fluorescence. It forms fluorescent solutions in alcoholic alkalis and concentrated acids, dyeing unmordanted wool in the alkaline bath red, which changes to greenish blue with acids and violet on washing with water. Prolonged heating of the hydrate of (*f*) with zinc-dust in alkaline solution converts it into the hydrate of (*g*), whilst the anhydrous compound itself, (*f*), is further dehydrated at 300° in carbon dioxide, with formation of anhydrous flavanthrinol (*g*). By means of a current of air, an alkaline solution of (*f*) readily passes into flavanthrene.

Flavanthrinol (*g*) may be obtained from its hydrate by heating to 160°, and forms red solutions with an olive-green fluorescence in concentrated acids, and dyes unmordanted wool violet-red, becoming green with acids and blue with water. Flavanthrinol requires to be heated in air or oxidised with ferricyanide before it will yield the original flavanthrene.

Another method of obtaining flavanthrene, though only in small yields, is described below (Scholl, Ber. 1910, 43, 1734). Dianthraquinonyl, on nitration, forms a mixture of dinitro derivatives, which by reduction with sodium sulphide give flavanthrene. By warming with sodium hyposulphite, a red solution is obtained, colouring unmordanted cotton light-blue in the bath, which changes in the air to flavanthrene yellow.

When flavanthrene is digested for 8 hours with a nitrating mixture, a yellow powder separates, $C_{28}H_8O_{10}N_6$, which appears to be dinitrodinitrosodihydroxyflavanthrene. This is reduced by ammonia and ammonium sulphide to tetra-aminodihydroxyflavanthrene, which, on warming with alkaline hyposulphite, yields a dark-blue vat, dyeing cotton a blue-black, which turns green with hydrochloric acid, owing probably to the formation of a hydrochloride, and again assumes a blue-black colour on washing with water, owing, no doubt, to dissociation (Ber. 1910, 43, 1748).

FLAVAURIN. A yellowish-red powder consisting of either the ammonium or sodium salt of dinitrophenolsulphonic acid, and obtained by boiling mononitrophenolortho- or para-sulphonic acid with dilute nitric acid (Leipziger Anilinfabr. Beyer und Kegel, D. R. P. 27271, June 8, 1883, expired October, 1886). Flavaurin dissolves readily in water, forming a yellow solution, and was introduced as a yellow dye for silk and wool.

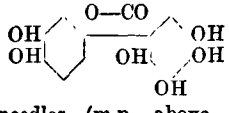
FLAVELLAGIC ACID $C_{14}H_6O_9$ is obtained in conjunction with ellagic acid when gallic acid is oxidised with potassium persulphate and strong sulphuric acid. By the employment of a dilute acid, flavellagic acid almost free from ellagic acid can be produced, and for this

purpose the following process is recommended (A. G. Perkin, Chem. Soc. Trans. 1906, 89, 251): 20 grams of gallic acid are treated with 160 c.c. of 96 p.c. sulphuric acid, 66 c.c. of water added, and the hot solution thus obtained is cooled to 50°, and maintained at this temperature during the gradual addition of 40 grams of potassium persulphate. A. G. Perkin and F. M. Perkin (Chem. Soc. Trans. 1908, 93, 1194) have obtained the same compound by the electrolytic oxidation of gallic acid in the presence of sulphuric acid.

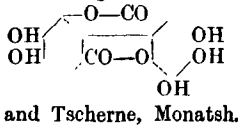
Flavellagic acid crystallises from pyridine in small yellow prismatic needles which contain pyridine, and does not melt below 360°. With nitric acid containing nitrous acid and subsequent dilution, it gives the blood-red colouration (Griessmayer reaction), which is also produced by ellagic acid. Dilute alkalis dissolve it with a yellowish-green colouration, and by distillation with zinc-dust *fluorene* is produced. *Acetyl flavellagic acid* $C_{14}HO_8(C_2H_3O)_5$, colourless needles, melts at 317°–319°, and *benzoylflavellagic acid* $C_{14}HO_8(C_7H_5O)_5$, prismatic needles, melts at 287°–289°. Flavellagic acid dyes mordanted woollen cloth shades somewhat resembling but stronger than those produced by ellagic acid.

Chromium	*Aluminium*	*Tin*	*Iron*
Yellowish olive	Pale greenish-yellow	Pale yellow	Dark olive-brown

By the action of boiling 50 p.c. potassium hydroxide solution, flavellagic acid gives *hexahydroxydiphenylmethylolid*



colourless needles (m.p. above 300°). This compound dissolves in solutions of the alkali hydroxides with an orange-yellow tint, and this, on dilution with water and exposure to air, develops a strong bluish-violet colouration. The acetyl derivative, $C_{13}H_2O_8(C_2H_3O)_6$, colourless prismatic needles, melts at 232°–234°. Flavellagic acid is hydroxyellagic acid, and possesses the following constitution:—



(*cf.* Herzig and Tscherne, Monatsh. 1908, 29, 281).

Flavellagic acid gives with diazomethane the *methyl ether* $C_{14}HO_4(OMe)_5$, m.p. 245°; and this is converted by methyl iodide and potassium hydroxide into *methyl-3:4:5:6:2':3':4'-heptamethoxydiphenyl-2:6'-dicarboxylate*

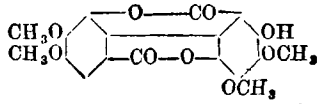
$$C_{12}H(OMe)_7(CO_2Me)_2$$

m.p. 83°–87°. The latter, on hydrolysis with potassium hydroxide, yields the *acid*

$$C_{12}H(OMe)_7(CO_2H)_2,$$

m.p. 163°–167°, in the anhydrous condition. From water it crystallises with $1H_2O$ and then melts at 95°–100° (decomp.) (M. von Bronneck, Monatsh. 1908, 29, 281).

When gallic acid 3:4-dimethyl ether, or gallic acid trimethylether is oxidised by means of potassium persulphate and sulphuric acid at 45° (Herzig and Schmidinger, Monatsh. 1910, 31, 918), *flavellagic acid tetramethylether*



yellow needles, m.p. 270°–271°, is produced, the acetyl derivative of which melts at 270°–271°. By means of methyl sulphate and potassium hydroxide, the heptamethoxy compound (described above) is obtained. A. G. P.

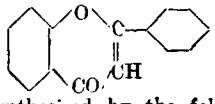
FLAVENOL *v.* QUINOLINE.

FLAVEOSINE *v.* ACRIDINE DYESTUFFS.

FLAVINE *v.* QUERCITRON BARK.

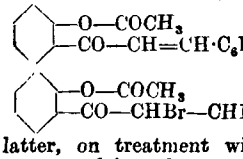
FLAVOLINE *v.* QUINOLINE.

FLAVONE, the mother substance of a large and very important group of natural colouring matters

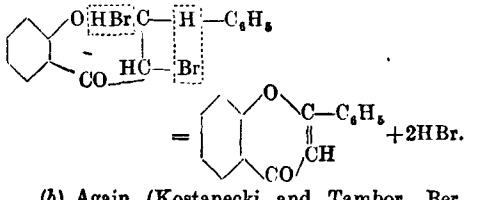


has been synthesised by the following three methods:—

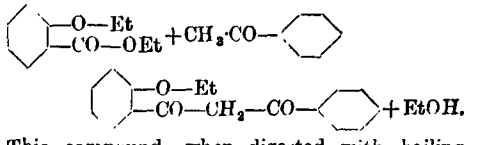
(*a*) *Acetyl-o-hydroxybenzylideneacetophenone* (I.) yields the *dibromide* (II.) (Feuerstein and Kostanecki, Ber. 1898, 36, 1757).



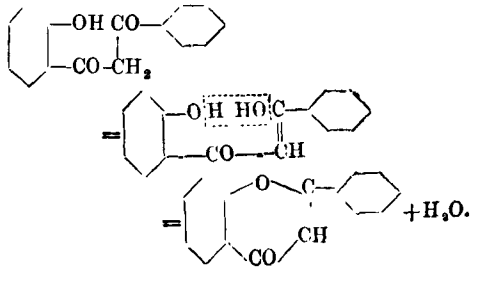
and the latter, on treatment with alcoholic potash, is converted into flavone, according to the following scheme:—



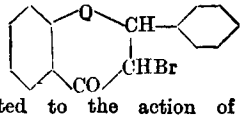
(*b*) Again (Kostanecki and Tambor, Ber. 1900, 33, 330) ethyl *o*-ethoxybenzoate and acetophenone, in the presence of sodium, give *o-ethoxybenzoylacetophenone*



This compound, when digested with boiling hydriodic acid, gives flavone



(*c*) Finally (Kostanecki and Sazbranski, Ber. 1904, 37, 2634), flavone is produced when *a-bromflavanone*

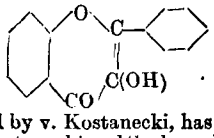


is submitted to the action of potassium hydroxide.

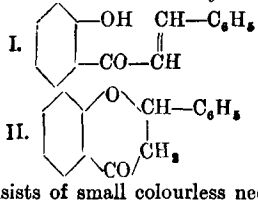
Flavone crystallises from ligroin in colourless needles, m.p. 97°, and is readily soluble in the usual organic solvents. Its solution in sulphuric acid is yellow, and possesses a weak blue fluorescence. A. G. P.

FLAVONOL. It is usual to subdivide the great family of yellow-colouring matters derived from flavone into two classes, *flavone* and *flavonol*, and the latter group is distinguished by the fact that the hydrogen of the γ-pyrone ring in these compounds is substituted by hydroxyl, whereas, in the former, it is not.

Flavonol.

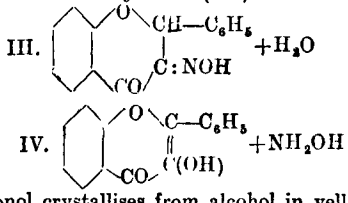


so designated by v. Kostanecki, has been synthesised by v. Kostanecki and Szabranski (Ber. 1904, 37, 2819) in the following manner. *Orthohydroxybenzylideneacetophenone* - (2 - *hydroxychalkone* (I.),) when digested with dilute alcoholic sulphuric acid, is converted into *flavanone* (II).



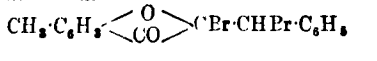
which consists of small colourless needles, m.p. 75°–76°.

By the action of amyl nitrite and hydrochloric acid in alcoholic solution, *isonitroso flavanone* (III.), crystalline powder, m.p. 158°-159°, is produced; and this, by means of boiling dilute mineral acids, splits off hydroxylamine and is converted into *flavonol* (IV.).

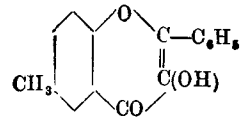


Flavonol crystallises from alcohol in yellow needles, m.p. 169°–170°. It forms a yellow liquid when warmed with aqueous sodium hydroxide, and its solution in sulphuric acid exhibits an intense violet fluorescence.

Acetylflavonol $C_{15}H_9O_3(C_2H_3O)$, colourless needles, melts at 110°–111°. According to Auwers and Müller (Ber. 1908, 41, 4233-4241), benzylidene cumaranones can be converted into flavonols. Thus benzylidene-4-methylcumaranone dibromide



when treated with potassium hydroxide gives *2-methylflavonol*



A. G. P.

FLAVOPURPURIN *v.* ALIZARIN AND ALLIED COLOURING MATTERS.

FLAX. This term, as applied to the fibre of commerce, designates the product of the plant *Linum usitatissimum* (Linn.), belonging to the nat. order *Linaceæ*, a group consisting of herbs and small shrubs indigenous to all temperate climates. *Linum usitatissimum* is now only found in its cultivated condition. The plant occurs in two main 'forms': *L. usitatissimum f. vulgare* or *indehiscens*, with a taller stem and fruits that do not split open spontaneously; and *L. usitatissimum f. humile* or *crepitans*, more richly flowered and with fruits that open spontaneously. The former form is cultivated for the production of fibre, the latter for the production of seed (linseed). The herb has a solitary erect stem, attaining a height of from 20 to 40 inches. The cultivation of flax is of insignificant extent in England and Scotland, but is of much greater importance in Ireland. It forms also an important crop in some parts of Belgium, Holland, France, and Russia.

The plant having attained about two-thirds of its full height, is ready for gathering; as when allowed to grow to maturity a coarser and less valuable fibre results. The stem consists of an internal woody core, an external cortex, and an intermediate cellular tissue (the bast), from which the flax is prepared. The operations necessary in the preparation of the fibre for the purposes of the spinner are (1) pulling; (2) rippling; (3) steeping, retting, or watering; (4) grassing; (5) breaking; (6) scutching; (7) heckling. Of these, 'pulling' is a distinctive method of gathering the flax plant, which is always torn up by the roots and not cut down like other crops. A fine day is selected for this purpose, and the stems are as far as possible arranged in sizes by the pullers; those also being assorted which may have been damaged by wind and rain. 'Rippling' is the process of removing the seed balls by drawing the heads through a species of comb set up usually in the field wherein the flax is being harvested. 'Retting' consists in immersing the stems in pools or streams of water in such a position that they shall stand almost erect, although weighted down so as to be quite submerged. The object of this is to induce fermentation, which dissolves the glutinous matter and disintegrates the fibres. Pure soft water and great judgment in the proper length of time to be allowed, which may be ten days to a fortnight, are essentials in this part of the treatment. Retting is followed by 'grassing,' whereby the separation of the flax fibre from the ligneous portions of the stalk is further facilitated. It consists in spreading the stems on the grass for a week or a fortnight, during which time they are occasionally turned. The flax during this operation becomes somewhat bleached. 'Breaking' and 'scutching' are the means employed to strip off the hard epidermis, and are

effected either by hand or machinery. 'Heckling' is a still further combing, which arranges the fibres in parallel order, ready for the manufacture of yarn.

According to Kolb, retting sets up a peculiar fermentation, which results in pectose or its analogous bodies being changed into pectin and pectic acid; of which the former being soluble is left in the water, whilst the latter being insoluble remains attached to the fibre until its treatment with hot alkaline lye in bleaching, when it is changed into soluble metapectic acid.

Under the microscope, flax fibre has the appearance of a cylindrical tube, not continuous as in the case of cotton, but broken up by septa or knots at irregular distances through the length of the fibre, varying from four to six times the diameter of the tube. This diameter is from about $\frac{1}{1703}$ to $\frac{1}{1505}$ of an inch. The adhesive power of the fibres, which gives the strength when spun into yarn, appears to depend on the twist given by the spindle as well as by the tenacity of the rough cellular sheath, which remains always more or less incrusted with the characteristic resinous deposit. Advantage is taken of the presence of this gummy deposit to detect the admixture in fabrics of cotton with linen; as, although the ultimate basis of both is cellulose, cotton exists in a much purer state than flax. The difference in the reaction upon them by caustic alkalis points out such admixture. When immersed in a boiling solution of caustic potash and water for about a minute, and then pressed between folds of filter paper, flax exhibits a dark-yellow colour, whilst cotton, when similarly treated, either remains white or becomes a very bright yellow. The same solution of potash employed cold colours raw flax orange-yellow, whilst cotton becomes grey, a result which Kuhlmann believed to be due to the pectic substances contained in flax.

FLINT. (Fr. *Silex*; Ger. *Feuerstein*.) A variety of chalcedonic silica, found chiefly in the Upper Chalk, where it occurs either as irregular nodules or in tabular masses, and more rarely in veins. It appears to be generally a mixture of opaline silica with microlites of quartz: hence it is acted upon unequally by solvents, the colloid silica being more soluble than the crystalline part. Organic remains, especially sponge spicules, are frequently enclosed in flint, and much of it seems to have been formed by the deposition of gelatinous silica around sponges: in other cases it may represent a silicified chalk-ooze. The nodules of flint are often hollow, sometimes lined in the interior with crystals of quartz, or with mamillated chalcedony, and enclosing fossils. Flint varies in colour from grey, yellow, and brown to black: according to Judd, the black colour is due to all the interstices of the flint being filled with colloid silica, while the white surface of an exposed flint is produced by removal of this interstitial silica in solution; the opaque white character of a calcined flint results from the formation of innumerable fissures throughout the mass (Proc. Geol. Assoc. 1888, 10, 219).

Flint differs from most other natural forms of silica by breaking with a conchoidal fracture, the fragments having sharp edges well suited for cutting. This character led to its extensive employment, before the introduction of metals, as a material for the implements and weapons of prehistoric man. Although brittle when first taken from its bed, it gradually loses moisture and acquires toughness. In many chalk districts, flint is used as a building stone and as a road material; while in the form of flint gravel and shingle it is largely employed elsewhere on roads. When struck with steel, or with iron-pyrites, sparks are elicited; whence the former use of flint in the tinder-box and in flint-locks. Gun-flints are still made to a limited extent, chiefly for the African market; the art of 'flint knapping' surviving at Brandon in Suffolk. When heated and thrown suddenly into cold water, flint may be easily pulverised; and the snow-white powder thus produced is used, as a pure form of silica, in the manufacture of pottery and glass.

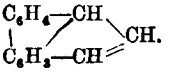
Large quantities of flint pebbles are also ground between blocks of chert for the same purpose. Most of this material is exported from France to England and America. From the chalk pits of Kent, Essex, Surrey, Sussex, and Hants about 30,000 tons of flint, valued at about 2*s*. per ton, are obtained per annum; and about the same amount is obtained in Belgium for the manufacture of pottery. L. J. S.

FLOS-FERRI *v.* ARAGONITE.

FLUID GELATIN *v. Aluminium oleate*, art. ALUMS.

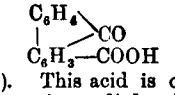
FLUORAL *v.* SYNTHETIC DRUGS.

FLUORANTHENE *Idryl*



Discovered independently by Fittig and Gebhard (Ber. 10, 2143; Annalen, 193, 142) in coal tar and by Goldschmiedt in 'stupp,' a mixture of hydrocarbons obtained in distilling mercury ores at Idria (Ber. 10, 2022). Obtained from the fraction of coal tar boiling higher than anthracene, by redistilling it at 250° under a pressure of 60 mm. A mixture of pyrene and fluoranthene passes over, which may be separated by repeated crystallisations from alcohol of their picric acid compounds; the fluoranthene picrate separates as long reddish-yellow needles, melting at 182°–183°. Forms slender needles or monoclinic plates, melting at 109°–110°; boils at 250°–251° under a pressure of 60 mm. Sparingly soluble in cold, readily soluble in boiling alcohol; soluble in ether, carbon disulphide, chloroform, benzene, and glacial acetic acid. Warm concentrated sulphuric acid dissolves the hydrocarbon, producing a deep-blue colour.

Chromic acid oxidises it to a quinone $C_{15}H_8O_2$ (red needles melting at 187°–188°), which, on further oxidation, yields *diphenyleneketone-carboxylic acid*

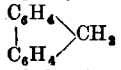


(m.p. 191°–192°). This acid is converted by heating with lime into *diphenylenketone* (*v.* FLUORENE), and by fusion with caustic potash into *isodiphenic acid* $\begin{matrix} C_6H_4\cdot COOH\ (1,2) \\ | \\ C_6H_4\cdot COOH\ (1,3). \end{matrix}$

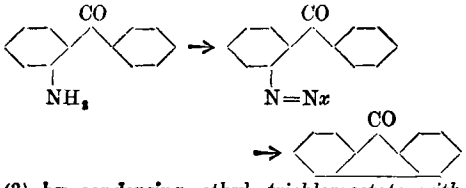
Fuming nitric acid forms with the hydrocarbon a trinitro derivative.

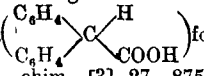
FLUOR-APATITE *v.* APATITE.

FLUORENE *o-Diphenylene methane*



Discovered by Berthelot in coal tar (Compt. rend. 65, 465; Ann. Chim. Phys. [4] 12, 222). Obtained (1) by passing the vapour of diphenylmethane through a red-hot tube (Gräbe, Annalen, 174, 194); (2) by reduction of diphenylene ketone either by distillation with zinc-dust (Fittig, Ber. 6, 187) or by heating with hydriodic acid and red phosphorus to 150°–160° (Gräbe, *ibid.* 7, 1625): the diphenylene ketone may be synthesised by splitting off H_2O and CO_2 from diphenic acid (Ostermayer and Fittig, *ibid.* 5, 935) or by diazotising *o*-amino-benzophenone and eliminating the diazo- group (Gräbe and Ullmann, *ibid.* 27, 3485)



(3) by condensing ethyl trichloracetate with benzene in the presence of aluminium chloride and heating to 290° the 9-fluorene carboxylic acid  formed (Delacre, Bull. Soc. chim. [3] 27, 875). The high-boiling fractions of tar oil after depositing naphthalene and anthracene are distilled; the fraction boiling between 295° and 310° contains the greater portion of the fluorene, which, on fusion with caustic potash at 280°, is converted into a solid potassium compound (Weissgerber, Ber. 34, 1659): the latter was originally separated mechanically from the fused hydrocarbons and the fluorene regenerated by treatment with water (D. R. P. 124150). Diphenylene oxide, present in the original mixture, is converted into potassium diphenate, and a small proportion of fluorene into *o*-phenylbenzoic acid; the alkaline mass is then treated with water and the hydrocarbons obtained pure by fractional distillation (D. R. P. 130679). The sodium compound, also used for the separation, is obtained by fusing the mixture of hydrocarbons with sodium or sodamide at 150°–200° (D. R. P. 203312). In the presence of aniline or other organic bases, the reaction proceeds more smoothly, and at a lower temperature (D. R. P. 209432). Recrystallisation from alcohol and glacial acetic acid, and precipitation of the picric acid compound (m.p. 81°), may be used in the purification.—Lustrous laminæ, melting at 115° (Delacre, *l.c.*). Boils at 294°–295° (corr.). Sparingly soluble in cold, readily in hot alcohol; readily soluble in ether, benzene, and carbon disulphide. Oxidation with lead oxide yields bisdiphenylene ethane and bisdiphenylene ethylene (red needles melting at 188°); with chromic acid diphenyleneketone (yellow prisms melting at 84°, boiling at 337°); with fused caustic potash *o*-phenylbenzoic acid and with potassium permanganate *o*-phthalic acid. With nitric acid (sp.gr. 1·4) in glacial acetic solution at 80°, 2-nitrofluorene is formed (Diels, Ber. 34, 1758); fuming nitric acid produces the 2:7-paradinitro derivative, melting at 199°–201° (Fittig and Schmitz, Annalen, 193, 134), 255°–260° (Barth and Goldschmiedt, Ber. 11, 846). The corresponding amino compounds have been used in the preparation of azo dyes, but do not yet appear to have found practical application. By the action of sulphuric acid and the halogens, substitution compounds are formed. The negative character of the methylene hydrogen atoms is shown by the formation of potassium and sodium compounds (*v. supra*), and by the formation of condensation products with benzaldehyde and oxalic ester (Thiele, Ber. 33, 851; Wislicenus, *ibid.* 33, 771). The conversion of phenanthrenequinone, by fusion with potash, to 9-oxyfluorene-9-carboxylic acid (Schmidt and Bauer, Ber. 38, 3738), and the formation of phenanthrene by a pyrogenic reaction from methyl fluorene (Gräbe, *ibid.* 37, 4145), furnish instances of the mutual conversion of 5 and 6 rings. Reduction with hydriodic acid yields a decahydrofluorene, $C_{16}H_{20}$ (Schmidt, *ibid.* 40, 4566); fluorene perhydride $C_{16}H_{22}$, is described by Spiegel (*ibid.* 41, 884; 42, 916).

Isomeric diphenylenemethanes were described by Carnelley (Chem. Soc. Trans. 1880, 708), who obtained them by passing the mixed vapours of benzene and toluene through a red-hot tube. I. S.

FLUORESCEÏN *v.* TRIPHENYL METHANE COLOURING MATTERS.

FLUORESCENT BLUE OR **RESORCIN BLUE** $C_{18}H_8Br_6N_2O_5(NH_4)$. A colouring matter obtained in 1880 by Weselsky and Benedikt by treating a solution of diazoresorufin in potassium carbonate with bromine, and precipitating with an acid. Soluble in boiling water, giving a reddish-violet solution with green fluorescence. On the addition of hydrochloric acid, the aqueous solution gives a yellowish-brown precipitate. With zinc-dust and caustic soda solution rapidly becomes colourless, but again becomes blue on exposure to air. Soluble in concentrated sulphuric acid with blue colour, which becomes violet on addition of water, and eventually gives a reddish-brown precipitate. Dyes silk and wool blue with brownish fluorescence (Brünner and Krämer, Ber. 17, 1847, 1867, 1875; Weselsky and Benedikt, Monatsh. 5, 605; Ber. 18, Ref. 76) (*v.* OXAZINE COLOURING MATTERS).

FLUORINE. Sym. F. At. wt. 19·0. Ampère, in 1810, first pointed out the analogy between hydrochloric acid and the gas evolved from a mixture of fluorspar and sulphuric acid; he assumed the existence of an element similar to chlorine, and further that the acid obtained from fluorspar was a hydrogen compound. Berzelius and Davy, a few years later, more fully established this view.

The name fluorine was given to the supposed element on account of its being a constituent of fluorspar. Many fruitless attempts had been made to isolate the element, but, owing to its great affinity for other elements, none could be regarded as successful until Moissan, in 1886, announced his results.

Occurrence.—Fluorine occurs in the combined state only, and generally as fluorspar CaF_2,

crystallising in cubes and octahedrons; this compound is found in abundance in Derbyshire, where it is known as Derbyshire-spar, and 'Blue John'; it is also found in Northumberland, Durham, Yorkshire, and Cornwall, and from it most of the preparations of fluorine are made. *Cryolite*, a double fluoride of aluminium and sodium $3NaF \cdot AlF_3$ or $Al_2F_6 \cdot 6NaF$, found in Greenland, is a mineral containing fluorine (*v.* CRYOLITE). Fluorine is widely but sparingly diffused, occurring in small amount in conjunction with aluminium and silicon in *topaz*; with cerium and yttrium in *fluocerite* and *yttrocerite*; it occurs also in *apatite*, *wavellite*, *wagnerite*, and other minerals. It is also found in the *idocrase* of Vesuvius, Christiansand in Norway, and in the variety from the River Wilui in Siberia (Jannasch, Jahr. Mineral. 1883, 2, 123). Traces of it exist in sea-water, and in the water of many mineral springs and rivers. Traces of fluorine have been detected by Wilson in the silicious stems of grasses and equisetaceous plants. Bones, both fossil and recent, contain fluorine (Carnot, Compt. rend. 1892, 114, 1189–1192), and it is found in the enamel of the teeth (Gabriel, Zeitsch. physiol. Chem. 18, 257–303, 1894; Wrampelmeyer, Zeitsch. anal. Chem. 32, 550–553, 1894). It is said to occur in the blood, the brain (Horsford, Annalen, 149, 202), and in milk, also in human urine.

Tammann (Zeitsch. physiol. Chem. 1888, 12, 322–326) has shown that fluorine is of great importance in the animal economy, while Saber Horstmann (Ann. Chim. Phys. 114, 510) has demonstrated that certain plants do not develop in its absence.

Isolation of fluorine.—Davy concluded, from his experiments on the compounds of fluorine, that the latter was an extremely active element. Since his time many chemists have endeavoured to obtain fluorine in the free state. It has been known since the time of Faraday that strong hydrofluoric acid is a very bad conductor of the electric current, and Moissan in his experiments found that the current from 50 Bunsen cells was not able to effect a passage through the anhydrous acid; by dissolving a little hydrogen potassium fluoride HF·KF in the acid, it was at once rendered a conductor. The apparatus employed consisted of an irido-platinum U-tube 9·5 cm. high and 1·5 cm. diameter (Fig. 1). At the side and near the top of each limb was a

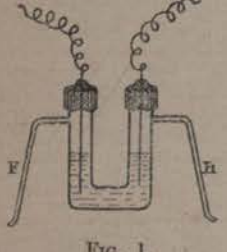


FIG. 1.

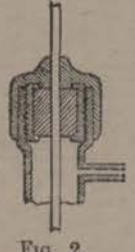


FIG. 2.

small exit tube of platinum, F and H; each limb of the U-tube was provided with a hollow cylinder screwed into it, and the hollow part of each cylinder was closed by a stopper of fluorspar, through the axis of which passed the terminals of iridio platinum (Fig. 2); these terminals were 2 mm. square in section and side, 12 mm. long, and passed to within 3 mm. from the bottom of each limb. The whole apparatus was first entirely freed from moisture by drying at 120°, then about 6 grams of the double fluoride of hydrogen and potassium were introduced, the stoppers screwed in and covered with shellac, and then

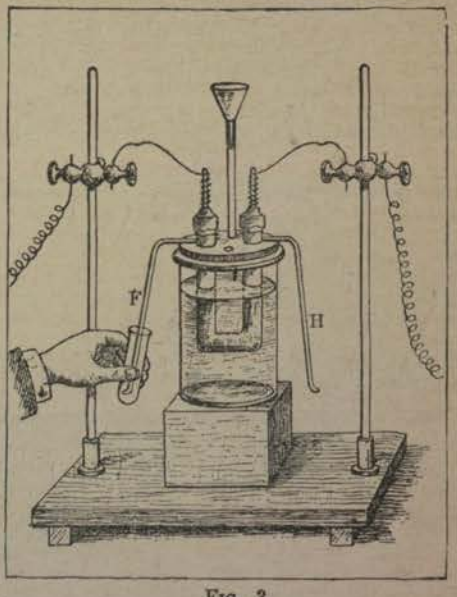


FIG. 3.

placed in a methyl chloride bath, a constant supply of which at −23° was maintained in the bath. The delivery tubes, hitherto kept in communication with desiccators of fused potash, are now connected with the vessel containing anhydrous hydrofluoric acid, and about 16 grams are gently aspirated into the apparatus. On now passing a current from 20 Bunsen cells through the solution, a continuous evolution of gas took place. To demonstrate its effects upon other bodies, they were placed in small glass tubes, and brought to the delivery tube at the positive side (Fig. 3).

On taking the apparatus to pieces after each experiment, the hydrofluoric acid remaining was found to contain a small quantity of platinum fluoride in solution, and a black mud consisting of a mixture of iridium and platinum in suspension. The negative electrode was not attacked, but the platinum rod forming the positive pole was eaten away to a point, so that one rod only served for two experiments. The average delivery of gas was about 1·5 to 2 litres per hour.

It is probable that potassium fluoride is first decomposed, fluorine being evolved at the positive pole, and potassium, which decomposes hydrofluoric acid, liberating its equivalent of hydrogen at the negative pole, reforming potassium fluoride which may be again electrolysed. Hence a small quantity of the double fluoride can serve for the decomposition of a comparatively large amount of hydrofluoric acid.

To prepare the pure anhydrous acid, a known volume of commercial acid was treated

with sufficient potassium carbonate to neutralise about a fourth part, and was then distilled in a leaden retort over an oil-bath at 120°. Potassium fluosilicate, formed from the hydrofluosilic acid contained as impurity, was not decomposed on distilling, and the distillate was therefore free from silica. The distillate was divided into two parts, one of which was neutralised by potassium carbonate and then added to the other half, thus forming the double fluoride HF·KF. This was dried at 100°, and kept for several days in vacuum in the receiver of the air-pump, over sulphuric acid and sticks of potash. When perfectly dry, this compound falls to powder, and is then ready for the preparation of the anhydrous acid. The dry fluoride thus obtained was introduced into a platinum retort and gently heated; the first portions of distillate are rejected, as they contain traces of water. A platinum receiver is then adapted and placed in a freezing mixture of ice and salt; on increasing the temperature, pure hydrofluoric acid passes over and is condensed in the receiver as a limpid liquid, which boils at 19·4°, is very hygroscopic, and fumes in air (Ann. Chim. Phys. [6] 12, 472–537).

The double fluoride is very soluble in hydrofluoric acid, forming with it a crystallisable compound richer in hydrofluoric acid than the double fluoride itself, and which gives off no acid vapour at the boiling-point of the anhydrous acid (19·4°).

Moissan electrolysed the double fluoride itself, which fuses at 140° to a colourless liquid. The experiment was done, as before, in a U-tube of platinum, but the latter was strongly attacked. On dipping the platinum terminals of the battery into the fused double fluoride contained in a platinum dish, gas was freely evolved at each pole, detonation occurring on bringing the terminals together, even in the dark. The wire at the end where the fluorine was evolved was strongly corroded.

Later Moissan found it possible to use an apparatus made of copper. The metal becomes coated with a film of fluoride CuF_2, which is insoluble and protects the copper from further corrosion. The electrodes must be made of platinum instead of copper, as the fluoride formed on the latter would diminish the current (Compt. rend. 1899, 128, 1543–1545).

Properties.—Fluorine is a gas of a penetrating and disagreeable smell, similar to that of hypochlorous acid. A column of the gas enclosed in a platinum tube 50 cm. long, with colourless fluorspar ends, has a decided greenish-yellow colour (Moissan, Compt. rend. 1890, 109, 937–940). Its dispersion is anomalous, being less at the blue end of the spectrum than it is at the red (J. H. Gladstone and G. Gladstone, Phil. Mag. 1891, [5] 31, 1–9).

The atomic refraction of fluorine, as determined from a number of its compounds for the line H of the solar spectrum, varies from 0·35 to 0·63, the numbers for chlorine, bromine, and iodine being 10·Q, 15·2, and 25·2 respectively (Gladstone, *l.c.*). For sodium light, the values 1·082 in unsaturated and 0·775 in saturated compounds (calculated according to the Lorentz formula) have been obtained by Swarts (Chem. Zentr. 1897, ii. 1042–1043). The atomic refraction of fluorine in unsaturated bodies is thus almost equal to that of hydrogen, so that if a double link is really present, fluorine has the smallest atomic refraction of any known element, its magnitude corresponding to its extremely low atomic volume, shown by Traube to lie between 0 and 1 (Annalen, 1896, 290, 105). The refractive index of the free element is 1·000195 for sodium light, being thus almost exactly one quarter that of chlorine, and bearing the same relation to it as do the refractive indices of nitrogen, oxygen, and neon to those of phosphorus, sulphur, and argon respectively. This value was obtained directly from measurement of the electrolytic gas, due allowance being made for oxygen, ozone, and nitrogen, which are always present (Cuthbertson and Prideaux, Phil. Trans. 1905, 205, A, 319–331).

The density of fluorine was determined after purification of the gas by passing it through a platinum worm cooled to −50° by methyl chloride, and thence through a tube containing anhydrous sodium fluoride, which removes the last traces of hydrogen fluoride. The volume of the gas was determined by analysis after interaction with water. The first determination was made in platinum vessels, and gave the value 1·265 (air) (Moissan, Compt. rend. 1890, 109, 861–864), but a later value, 1·310, obtained by the Regnault method in a glass vessel (Moissan, *ibid.* 1904, 138, 728–632), corresponds almost exactly to the value 1·319, calculated from the atomic weight F=19·05 and molecular weight 38·10. The possibility of the existence of any measurable proportion of free fluorine atoms is thus excluded.

Fluorine was liquefied by Moissan and Dewar in 1897 (Compt. rend. 1897, 124, 1202–1205) by subjecting the gas to the cooling action of liquid oxygen, boiling under reduced pressure. Liquid fluorine is of a yellowish colour and very mobile. When placed in liquid hydrogen, it forms a white solid, m.p. −223° (Moissan and Dewar, Compt. rend. 1903, 136, 641–643). The critical temperature of fluorine is about 120°; the critical pressure, about 40 atmospheres; and the boiling point, −187°. The density of liquid fluorine is about 1·14. Its specific refraction is greater than that of liquid air or oxygen, its capillary constant less than that of liquid oxygen. It has no magnetic properties, and shows no specific absorption bands (Moissan and Dewar, Chem. Soc. Proc. 1897, 175).

Fluorine gas has an irritating effect on the eyes and upon the mucous membrane. It decomposes water with formation of hydrofluoric acid, and the oxygen which is set free is ozonised. It corrodes glass, and attacks with violence all organic compounds, cork being at once carbonised and inflamed; alcohol, ether, benzene, and turpentine take fire immediately in contact with it.

Fluorine, freed from hydrofluoric acid by subjection to the temperature of boiling air and subsequent passage over dry sodium fluoride cooled by a solution of solid carbon dioxide in acetone, does not attack glass even at 100°, provided that the surface of the glass is free from all traces of organic matter. It is impossible to dry fluorine by means of phosphorus pentoxide, as phosphoryl trifluoride is immediately formed (Moissan, Compt. rend. 1899, 129, 793–804).

Fluorine combines with hydrogen, even in the dark, the combination is attended with detonation, and is effected even at the temperature of liquid hydrogen (Moissan and Dewar, *ibid.* 1903, 136, 641–643). Iodine burns in fluorine with a pale-blue flame, forming iodine pentafluoride (Moissan, *ibid.* 1902, 135, 563), and, in an atmosphere of iodine vapour, fluorine burns with a similar flame. Vapour of bromine loses its colour in fluorine, and the combination is sometimes attended with detonation with formation of bromine trifluoride (Lebeau, *ibid.* 1905, 141, 1015; Prideaux, Chem. Soc. Trans. 1906, 316). Fluorine at once releases chlorine from cold potassium chloride; chlorine is also expelled from its combination with carbon in carbon tetrachloride, but does not unite with fluorine.

Nitrogen also has no action on the gas, but excess of fluorine acts upon nitric oxide at the temperature of liquid oxygen, forming nitroxyl fluoride, m.p. −139°, b.p. −63·5°, density 2·17–2·31, a colourless gas at the ordinary temperature (Moissan and Lebeau, Compt. rend. 1905, 140, 1621–1626).

Sulphur, selenium, and tellurium, on being placed in fluorine, at once melt and inflame with incandescence and formation of fumes and a coating of solid fluorides. Phosphorus burns in it with formation of fluoride and oxyfluoride; arsenic in powder becomes incandescent, and forms liquid drops of the trifluoride; antimony also becomes incandescent. Silicon in crystalline form, and cold, burns with brilliancy, and sometimes with scintillations. Adamantine boron also burns in the gas.

Metals are all attacked, but with varying energy, and formation of fluorides. Sodium and potassium in the cold are rendered incandescent. Calcium, magnesium, and aluminium become incandescent when slightly warmed. Iron and manganese in a state of powder, with slight warming, burn with bright scintillations. Lead is attacked in the cold, and tin on slightly warming. Mercury is entirely converted into a yellow protofluoride. Silver, at a gentle heat, becomes coated with a satin-like deposit of fluoride soluble in water. Gold and platinum, when heated to between 300° and 400°, become converted into their respective fluorides, which are decomposed again at a red heat with evolution of free fluorine (Ann. Chim. Phys. 1887, [6] 12, 472–537; Moissan, Fluorine et ses composés). Even at −187°, liquid fluorine reacts with a large number of substances. Sulphur, selenium, arsenic, phosphorus, potassium, calcium oxide, and anthracene all react violently with it, while solid fluorine combines with liquid hydrogen at −252·5°, with violent explosion, sufficient heat being evolved to render the materials incandescent (Moissan and Dewar, Compt. rend. 1903, 136, 641–643). If, however, sulphur, phosphorus, carbon, silicon, boron, and iron be first cooled in liquid air, they do not react with fluorine at −185°, neither is iodine displaced from iodides at this temperature, nor glass corroded (Moissan and Dewar, *ibid.* 1897, 124, 1202–1205). If fluorine be passed into liquid oxygen, a flocculent precipitate collects, which deflagrates on rise of temperature. It is probably a hydrate of fluorine, as it is never obtained from perfectly dry oxygen.

The majority of the metallic compounds of fluorine are easily fusible, and when ignited in a current of steam many of them are converted into the corresponding oxides, whilst hydrofluoric acid is formed. The fluorides of silver and tin are easily soluble in water, while those of sodium, potassium, and iron are only sparingly soluble. They are all decomposed by sulphuric acid when heated, with evolution of hydrofluoric acid, but nitric does not so easily attack them. Heated in a current of chlorine, they are all decomposed with formation of corresponding chlorides. Solutions of the soluble fluorides corrode glass, and they give no precipitate with silver nitrate, as the fluoride of silver is soluble. Lead, barium, magnesium, and calcium salts produce insoluble precipitates. The precipitate of calcium fluoride is so transparent as to be perceived with difficulty, but is rendered more opaque by heating.

Many metallic fluorides combine with hydrofluoric acid and form compounds obtainable in crystals soluble in water. The double fluorides of the alkali-metals with the fluorides of the electro-negative metals which form acids with oxygen may be obtained with facility, and are analogous in composition to the double fluoride of hydrogen and potassium. They are all decomposed by sulphuric acid, yielding hydrofluoric acid and a sulphate. A mixture of hydrofluoric acid and nitric acid dissolves silica which has not been previously ignited, but the mixture has no action on gold or platinum.

The atomic weight of fluorine.—With two notable exceptions, all the determinations of the atomic weight of fluorine involve the conversion of fluorides of various metals into the corresponding sulphates, the fluoride most commonly employed being that of calcium, which was used in some cases in the form of a very pure fluorspar.

Berzelius (Poggendorff's Annalen, 1826, 8,1), Louyet (Ann. Chim. Phys. 1849, [3] 25, 295), Dumas (Annalen, 1860, 28, 113), De Luca (Compt. rend. 1860, 51, 299), and Moissan (*ibid.* 1890, 111, 570–572) all made use of this method, the average weight of calcium sulphate obtained from one part of fluoride being 1·7444±0·00018 gram, which gives 18·999 as the atomic weight of fluorine.

Louyet, by the conversion of lead fluoride into lead sulphate, obtained the value 19·01; Moissan, working with barium fluoride, obtained the value 19·02. Dumas, Louyet, and Moissan (Compt. rend. 1890, 111, 570–572) also worked with sodium fluoride, the results by this method being uniformly higher, viz. 19·08, 19·06, and 19·07 respectively. Values were also obtained by Dumas and Moissan from the conversion of potassium fluoride into potassium sulphate.

An exceptional method was employed by Christensen (J. pr. Chem. 1886, [2] 34, 41–46), who took advantage of the decomposition of ammonium manganifluoride $(NH_4)_2MnF_5$ to measure the atomic weight of fluorine. The manganifluoride was treated with potassium iodide, one molecule of the former, on acidification with hydrochloric acid, liberating a molecule of iodine, which was then titrated with standard sodium thiosulphate solution. In the first series of experiments, he obtained the value F=19·00, and in the second (J. pr. Chem. 1887, [2] 35, 541–559) F=18·99.

Meyer (Zeitsch. anorg. Chem. 1903, 36, 313–324) compared the results of these previous investigations, criticising both the suitability of the methods and the purity of the materials employed. To the latter cause he mainly attributed the discrepancies in the values obtained. He therefore started with pure ammonium carbonate and calcium nitrate, converted the calcium carbonate so obtained into oxide, which he slaked and converted into chloride, and passed finally to fluoride by evaporation of the chloride with specially purified hydrofluoric acid. As the mean of 5 determinations, he obtained the value F=19·036, error ±0·00149. The general mean of all the determinations agrees well with the results of Christensen and Meyer, if all the values are recalculated with the most recent atomic weights (F. W. Clarke, Recalculation of Atomic Weights, 1910). The mean value for the atomic weight of fluorine is 19·041 ± 0·00135; the recalculated results of Christensen give an average value of 19·038, and those of Meyer 19·035.

Additional confirmation of Christensen's value is obtained from the fact that the atomic weight of manganese, Mn=54·933, calculated from his data, agrees well with that obtained by Baxter and Hines (J. Amer. Chem. Soc. 1906, 28, 1560).

Comparison of fluorine with the other halogens.—Fluorine is by far the most energetic member of the halogen family, and, as is frequently the case with the first member of a series, it possesses very distinctive properties. Moissan has pointed out (Bull. Soc. chim. 1892, [3] 5, 880–885) that in certain of its relations, it remotely resembles oxygen rather than chlorine. Thus carbon readily takes fire and burns in it (Moissan, Compt. rend. 1890, 110, 276–279). Calcium fluoride is very different from calcium chloride, rather resembling calcium oxide in solubility. Silver fluoride is also anomalous, being easily soluble in water, while aluminium fluoride is much less easily hydrolysed than is the chloride.

Fluorine compounds with the non-metals are uniformly more volatile than the chlorine compounds, but the metallic fluorides usually require a higher temperature for fusion than do the other halides.

The boiling-point of a hydrocarbon is increased on the average by 5° by the substitution of fluorine for hydrogen, but if fluorine is introduced into a molecule already containing halogen atoms, the boiling-point is lowered, the same behaviour being observed in the case of aldehydes. In this respect, fluorine differs greatly from chlorine (Henry, Rec. trav. Chim. 1897, 16, 218–225; Moissan and Dewar, Chem. Soc. Proc. 1897, 175).

Hydrofluoric acid or **Hydrogen fluoride** HF. The corrosive action of this compound on glass was known to Schwanhardt of Nuremberg as early as the year 1670. Scheele, in 1771, first recognised that fluorspar is a compound of lime and a peculiar acid, and he prepared the latter in both the aqueous and gaseous forms by distilling in a tin retort. Priestley was the first to collect the gas over mercury. It was regarded by Gay-Lussac and Thenard, in 1808, as an oxygen compound. Ampère, however, in 1810, pointed out its similarity to hydrochloric acid, a view which was subsequently supported and confirmed by Davy and Berzelius. It was first obtained in a pure state by Gore in 1868.

Its volumetric composition can be shown either by electrolysing the acid and collecting and measuring the liberated hydrogen and oxygen, or by allowing a measured volume of fluorine to act on water, titrating the acid formed, and measuring the oxygen. In both cases, after allowing for the contraction in the volume of oxygen, due to formation of ozone, the results show that hydrogen fluoride is formed by the union of equal volumes of hydrogen and fluorine (Moissan, Compt. rend. 1900, 130, 544–548; *cf.* mol. wt., Gore, below).

The anhydrous acid is best prepared from the double fluoride of potassium and hydrogen, as previously described. Fremy obtained the anhydrous acid by decomposing lead fluoride with dry hydrogen.

Anhydrous hydrofluoric acid is a colourless, mobile liquid of density 0·9879 (Gore). It boils at 19·4°, and solidifies at −102·5° to a white crystalline transparent mass, becoming white and opaque at a lower temperature, and melts at −92·3° (Olszewski, Monatsh. 1886, 7, 371–374). Its vapour tension at 15·5° is equal to a pressure of 7·58 lbs. per square inch. The anhydrous acid does not attack glass even if left in contact with it for weeks; but if the least trace of moisture be present, this action is apparent at once. The acid has little action on the metalloids and the noble metals, and below 20° the other metals are not attacked. Basic oxides unite readily with it, some of them dissolving; on peroxides it has no effect.

Potassium, when thrown into the anhydrous acid, decomposes it with explosion. It combines eagerly with phosphoric and sulphuric anhydrides, with evolution of great heat, in this respect resembling water, and not its more obvious analogue, hydrochloric acid. It also combines energetically with the fluorides of potassium and sodium, just as water combines with the oxides of these metals.

The anhydrous acid decomposes carbonates with effervescence and with the formation of fluorides. Solid organic bodies immersed in it are for the most part disintegrated. Gutta-percha, caoutchouc, and numerous gums and resins dissolve to red liquids. Guncotton, silk, paper, cotton wool, calico, &c., are converted into glutinous substances, and generally dissolve. Wood spirit, alcohol, and ether, but not benzene, mix with it, and oil of turpentine, when mixed with it, forms a red liquid (Gore, Proc. Roy. Soc. 17, 256).

The molecular weight of hydrogen fluoride has been a source of some controversy. Gore (Phil. Trans. 1869, 73) showed that the volume of hydrogen fluoride gas obtained by the action of hydrogen on silver fluoride was twice that of the hydrogen taken, the measurements being made at 100°, but Mallet, weighing the gas at 30·5° in a large flask coated with paraffin, obtained a value for the density corresponding to a molecular weight of 39·32, which indicates the molecular formula H_2F_2 (Amer. Chem. J. 1881, 3, 189).

Thorpe and Hambly (Chem. Soc. Trans. 1889, 163) find that the vapour density of hydrogen fluoride varies rapidly with the temperature and pressure. The following table gives the

results of their experiments at temperatures varying between 26·4° and 88·1° :—

Temperature	Pressure mm.	V.D. air=1	Mol. weight
26·4°	745	1·773	51·18
27·8	746	1·712	49·42
29·2	750	1·578	45·54
32·0	743	1·377	39·74
33·1	750	1·321	38·12
33·8	758	1·270	36·66
36·3	739	1·115	32·20
38·7	751	1·021	29·46
39·2	743	1·002	28·94
42·8	741	0·910	26·26
47·3	745	0·823	23·76
57·5	750	0·737	21·28
69·4	746	0·726	20·96
88·1	741	0·713	20·58

These numbers show that the process of dissociation of the vapour of hydrogen fluoride is perfectly continuous, and that there is no direct evidence of the existence of a molecule corresponding to H_2F_2. It is also found that the vapour density is lowered by diminishing the pressure of the gas at a constant temperature. The following table shows the vapour density of hydrogen fluoride under varying pressures at the constant temperature of *circa* 32° :—

Temperature	Pressure mm.	V.D. air=1	Mol. weight
32·0°	743	1·377	39·74
32·2	686	1·239	35·78
31·8	655	1·177	33·98
32·0	603	1·068	30·82
32·5	545	0·963	27·78
32·3	498	0·920	26·54
31·9	354	0·797	23·00
32·3	353	0·789	22·78

Similar results were obtained by mixing the hydrogen fluoride with air so as to lower the partial pressure of the gas.

The anhydrous acid, on addition of water, is changed in sp.gr. from 0·988 to as much as 1·25, further dilution causing a regular decrease in sp.gr. (For a table showing the relation between the sp.gr. and strength of hydrofluoric acid, *v.* Winteler, Zeitsch. angew. Chem. 1902, 15, 33–34; J. Soc. Chem. Ind. 1902, 277.) The acid of sp.gr. 1·15 may be distilled unchanged; it boils at 120°, and contains about 36 to 38 p.c. of the anhydrous acid, but does not thus form a definite hydrate; when allowed to evaporate over caustic lime in the air, the aqueous acid attains a constant composition containing 32·6 p.c. of the anhydrous acid (Roscoe, Chem. Soc. Trans. 1861, 13, 162).

According to Deussen (Zeitsch. anorg. Chem. 1906, 49, 297–300), a constant boiling mixture of boiling-point 111° at 750 mm. pressure has a sp.gr. of 1·138 at 18° and contains 43·2 p.c. hydrofluoric acid by weight.

Hydrogen fluoride gas is formed from its elements with great evolution of heat :

H gas + F gas=HF gas +37·6 cals.

H gas + F gas=HF (dissolved)+49·4 cals.

(Berthelot and Moissan, Compt. rend. 1889, 109, 209). (For heat of dissolution, *cf.* Guntz, Bull. Soc. chim. 1884, 40, 54–57.) The dilution of acid containing more than two molecules of water does not produce a sensible evolution of heat, as does similar dilution of the other halogen acids (Guntz, *l.c.*).

Hydrofluoric acid is also unique in that it combines with its own salts with absorption of heat NaF+HFAq. = −288 (Thomsen). The freezing-point of water is depressed by hydrofluoric acid, and quantitative determinations point to the existence of molecules of H_2F_2 in solution (Abegg, Fox, and Herz, Zeitsch. anorg. Chem. 1903, 35, 129–147; Paternò and Peratoner, Chem. Zentr. 1891, 306).

This view is supported by the fact that the heat of dissociation of hydrofluoric acid is 3550 cals., which is three times the corresponding value for hydrochloric acid, and is most easily explained by assuming the preliminary dissociation $H_2F_2 \rightleftharpoons 2HF$ (Abegg, Ber. 1900, 33, 393–394), and further evidence is obtained from the fact that by the application of Ostwald's basicity rule, the value for the basicity =2·08. This observation is confirmed by measurements of specific conductivity after the addition of successive quantities of potassium, sodium, and ammonium hydroxides (Pellini and Pegoraro, Zeitsch. Elektrochem, 1907, 13, 621). Acid, containing 55 p.c. hydrogen fluoride, cooled to −45°, is converted into small truncated prisms, having the composition HF,H_2O and melting at −35° (Metzner, Compt. rend. 1894, 119, 682–684). Other evidence as to the existence of hydrates is derived from the relation of the specific conductivities of different solutions of hydrofluoric acid to the corresponding concentrations. It is found that breaks in the curve obtained by plotting these values occur at concentrations of 91 p.c., and between 51 and 55 p.c. corresponding to the hydrates 9HF, H_2O, and HF,H_2O (*cf.* Metzner, *l.c.*; Hill and Sirkar, Proc. Roy. Soc. 1909, A, 83, 130–148).

The temperature coefficient of conductivity for solutions containing less than 7·7 p.c. HF =0·0125 and is constant. Hydrofluoric acid can be electrolysed with platinum as a positive electrode, the products being hydrogen, oxygen, and ozone, but with acid of 30 p.c. strength, the platinum is attacked.

The dilute acid dissolves all the metals except platinum and some of the metals associated with it—gold, silver, lead, and mercury—with evolution of hydrogen. On this account, it is kept in platinum vessels when concentrated, and in leaden or guttapercha vessels in the dilute form.

Aqueous hydrofluoric acid may be kept in glass bottles coated with a film of guttapercha as follows. Guttapercha is dissolved in carbon disulphide and the solution put in a bottle, every part of the interior of which must be brought in contact with the solution; the excess, if any, is then poured out, and the bottle laid aside until the solvent has volatilised. Caoutchouc stoppers are required (Chem. News, 49, 201).

On mixing one part of finely powdered and pure fluorspar with about twice its weight of strong sulphuric acid, no evolution of gas takes place at ordinary temperatures, but a transparent gelatinous mass is formed, and, on

gently heating, dense and highly irritating fumes arise, somewhat similar to those produced in the manufacture of hydrochloric acid: $CaF_2+SO_4H_2=SO_4Ca+2HF$. For ordinary purposes, the decomposition is effected in a leaden retort, divided into two halves for convenience in cleaning, which, when in use, are accurately fitted together by an overlapping grooved joint. The receiver may be a leaden V-tube, blind at one end, and fitted by grinding at the other to the neck of the retort; the retort is heated on a sand-bath, and the acid is condensed in the receiver, which is surrounded by a freezing mixture.

To prepare the aqueous solution on a large scale, a leaden retort, on the upper part of which a leaden head can be cemented, is used; the neck of the retort fits into the side of a leaden receiver or chamber, in which is placed a basin of water. The acid vapours are absorbed by the water, and air, with any excess of acid vapours, is conducted through an escape pipe into the atmosphere.

The impure commercial acid may be purified by passing an excess of hydrogen sulphide through the liquid, neutralising the sulphuric and silicofluoric acids present with potassium carbonate, then decanting and adding silver carbonate to remove excess of hydrogen sulphide, filtering, distilling the filtrate from a leaden retort with a platinum receiver, and finally rectifying. As in the case of fluorine itself, copper can readily be employed as the material of the containing vessels (Goldschmiedt, Monatsh. 1907, 28, 297–298).

Use of hydrofluoric acid.—The chief use of this compound is in etching glass. In making the graduations on a thermometer the tube is first coated with engravers' etching varnish; the divisions are then accurately traced with a fine-pointed instrument through the varnish. The tube is then plunged for a short time into a long tube containing dilute hydrofluoric acid, when, after cleaning the thermometer tube, it will be found to be permanently engraved. If the engraving is done by the vapour of hydrofluoric acid, the tracings are white and opaque, whereas if the liquid acid be employed, the lines are transparent.

There are three processes in use for the preparation of opaque etchings on glass: viz. (*a*) the application of solutions of acid fluoride of the alkalis; (*b*) a mixture of fluorspar with sulphuric acid; and (*c*) hydrofluoric acid gas. The first of these always contains uncombined hydrofluoric as well as an indifferent salt as shown in the following recipes:—

—	I.	II.		III.	
	grms.				
Water	1000	100	1000	1000	1000
Acid potassium fluoride	250	—	—	—	—
Sodium fluoride	—	—	40	250	—
Ammonium fluoride	—	—	—	—	1000
Alkali fluoride	—	8	—	—	—
Hydrochloric acid	250	—	—	160–175	—
Sulphuric acid	—	1	—	—	250
Glacial acetic acid	—	—	50	—	—
Potassium sulphate	140	—	—	200	—
Ammonium sulphate	—	—	—	—	100

The first of these recipes is recommended by Tessié du Mothay and Maréchal; the two under heading II. by Siegwart, and those under heading III. by J. B. Miller. In practice, however, an acetic solution of sodium fluoride is much used, and is prepared by dissolving 25 parts of sodium carbonate crystals in 5 parts of fuming hydrofluoric acid, and adding to 1 litre of this solution after clarifying, 1 litre of glacial acetic acid. For light shades of etching, a single application of the acid is sufficient, but for deeper shades repeated applications are necessary, as is the case in etching landscapes, &c., on glass. An etched glass surface viewed by the microscope has the appearance of an aggregation of crystals, hexagonal in shape, and agrees with those of silicon-sodium fluoride, and in addition there are some longer in shape, which much resemble those of silicon-calcium fluoride. Small crystals are formed from concentrated solutions, and the smaller the crystals the more delicate is the etching. The strength of an etching solution must be varied according to the compound used, and regard must also be paid to the kind of glass to be operated upon. The application of gaseous hydrofluoric acid does not produce a uniform opacity, and is, therefore, not suitable for the production of opaque plates (J. Soc. Chem. Ind. 5, 669).

It has been suggested that hydrofluoric acid should be employed in the purification of beet sugar, the alkalis present in the juice being effectually removed by the acid, whilst the organic matter remains unaffected (*cf.* Verbiese, J. Soc. Chem. Ind. 1900, 160).

Antiseptic properties of fluorine compounds.—W. Thompson found that the compounds of fluorine, such as hydrofluoric acid, the acid and neutral fluorides of sodium, potassium, and ammonium (as well as the fluosilicates of these bases), are effectual as antiseptics. Free hydrofluoric acid retards the activity of yeast, 5·5 mgm. per 100 c.c. of saccharine solution arresting fermentation. Potassium fluoride, up to the same strength, however, augments it (Effront, Bull. Soc. chim. 1891, [3] 5, 476–480). The free acid promotes the activity of diastase by retarding lactic and butyric fermentations (Effront, *ibid.* 1891, 4, 337–339; 627–632; 1892, 6, 786–793), and its application in breweries has been suggested (Just, J. Soc. Chem. Ind. 1902, 131). Acid ammonium fluoride is especially used for disinfecting rubber hose-pipes in breweries, as it is a powerful antiseptic and does not attack the rubber (Schonfeld, J. Soc. Chem. Ind., 1901, 830; Brand, *ibid.* 1904, 265; Bidtel, *ibid.* 1904, 620).

Fluorides have also been used as preservatives for sweet wines and beer, sodium fluoride having been put on the market for this purpose under the name 'Remarcol.'

Tests for hydrofluoric acid.—For the detection of this compound, its corrosive action on glass is utilised. The compound suspected to contain a fluoride is reduced to powder and moistened with strong sulphuric acid in a platinum or leaden capsule. A watch-glass is thinly coated with wax, and, after tracing some design with a sharp-pointed instrument, is inverted over the capsule. The capsule is then gently warmed and the watch-glass placed over it, a little water being put in to prevent the melting of the wax.

On removing the watch-glass after a few minutes' exposure, and cleaning off the wax with a little oil of turpentine, the parts exposed will have become etched if fluorine was present in the mixture. When the etching is very faint, a good plan is to breathe upon it, which makes the markings more apparent.

In the absence of boron, this test can be made more delicate by placing the suspected substance, mixed with quartz powder and a little magnesite, in a test-tube fitted with a cork, carrying a glass rod having a knob at the lower end. This knob is painted black and a drop of water is placed on it. On adding conc. sulphuric acid to the mixture in the tube and warming cautiously, a white film will be seen if as little as 0·1 mgm. of fluorine is present (Daniel, Zeitsch. anorg. Chem. 1904, 38, 257).

For the detection of fluorine in butter, the aqueous portion from 50 grams of melted butter is treated with calcium chloride solution and a small excess of sodium carbonate. The resulting precipitate, consisting probably of borate, carbonate, phosphate, sulphate, and fluoride, is extracted with acetic acid, ignited and heated on a sand-bath with sulphuric acid, under a waxed watch-glass cooled by water on its upper surface for 2 hours. 1 mgm. of calcium fluoride will, under these circumstances, give a distinct etching on glass (Hehner, Analyst, 1902, 27, 173–179).

For methods of estimating fluorine *v.* ANALYSIS.

Silicon fluoride may be estimated by measurement, in a dry gas burette, of the volume of gaseous silicon fluoride produced by the interaction of quartz, fluoride, and sulphuric acid (Oeltel, Zeitsch. anal. Chem. 1886, 25, 505; Hempel and Scheffler Zeitsch. anorg. Chem. 1899, 20, 1–11).

Hydrofluoric acid may be estimated by the amount of etching produced (Ost, Ber. 1893, 26, 151; Wislicenus, Zeitsch. angew. Chem. 1901, 706; Leiniger, Chem. Zeit. 1902, 26, 967; Woodman and Talbot, J. Amer. Chem. Soc. 1906, 28, 1437–1443).

Fluorine in soluble fluorides can be estimated volumetrically by taking advantage of the fact that ferric fluoride, unlike ferric chloride, does not liberate iodine from iodides. The liquid is acidified with hydrochloric acid, mixed with a known excess of ferric chloride solution, then with excess of zinc iodide, allowed to remain in a closed vessel at 35°–40° for half an hour, and the liberated iodine titrated with sodium thiosulphate solution (Knobloch, Chem. Zentr. 1894, ii. 533–534).

For the estimation of fluorine in wine, a standard method has been worked out, as fluorine preservatives are so frequently used. 100 c.c. of wine are made feebly alkaline with sodium hydroxide, silver nitrate is added, so long as it produces a precipitate, and the solution made up to 250 c.c. and filtered. 200 c.c. of the filtrate are treated with excess of sodium chloride, made up to 250 c.c. and left for 24 hours. 175 c.c. of clear liquid are treated with 3–4 c.c. 2N-sodium carbonate solution and precipitated with a large excess of calcium chloride solution and boiled for 5 minutes. The precipitate is collected and ignited and digested with 24 c.c. of 3/2N-acetic acid until its weight is constant within 5 milligrams. For each 100 c.c. of washings, 0·0016 gram is added to correct for solubility (F. P. Treadwell and Koch, Zeitsch. anal. Chem. 1904, 43, 469–506). For beer, a slight modification of Penfield's method (Chem. News, 1897, 39, 79–180) is recommended.

Silicofluoric acid or Hydrofluosilicic acid H_2SiF_6. This compound is prepared by heating a mixture sulphuric acid and fluorspar, sand, or powdered glass in a flask and passing the evolved silicon fluoride into water $3SiF_4+2H_2O=SiO_2+2(H_2F_2{\cdot}SiF_4)$. The tube from which the fluoride escapes must dip into mercury at the bottom of the vessel of water, otherwise it would soon be stopped up by the deposition of silica. The bubbles of gas as they rise through the water are decomposed, and a gelatinous mass accumulates. The solution of acid is strained through linen to separate the silica, and is then filtered and concentrated at a low temperature. The acid is obtained more easily when required in quantity by dissolving silica in dilute hydrofluoric acid. The saturated solution fumes strongly, and has a very sour taste. It does not attack glass, but if allowed to evaporate on it the glass is attacked, especially on heating; silicon fluoride is volatilised, and the free hydrofluoric acid attacks the silica of the glass. The salts are called silicofluorides or fluosilicates, are generally soluble in water, and may be obtained well crystallised. The potassium salt is one of the least soluble salts of potassium, and the copper salt one of the most soluble of copper salts. Silicofluoric acid is sometimes employed as a test for potassium.

Hydrofluosilicic acid reacts with potassium ferrocyanide, epecially in boiling solution, forming a greenish liquid, which, on contact with air, deposits a precipitate of Prussian blue. The same reaction takes place with the ferricyanide, but in the absence of air (Materschek, Chem. Zeit. 1901, 25, 158; 327). Calcareous stone surfaces can be hardened by means of a fluosilicate of some metal which forms an insoluble oxide, such as magnesium, aluminium, or lead. Carbon dioxide is given off, and calcium fluoride, silica, and alumina, or the carbonate of lead or magnesium fluoride, are formed, and the surface rendered hard and insoluble (Kessler, Compt. rend. 1883, 96, 1317–1319).

For modes of estimating hydro-fluosilicic acid *v.* ANALYSIS.

Antiseptic properties.—The fluosilicates pos sess more powerful antiseptic properties than the fluorides. They are not poisonous, possess no smell, and are sparingly soluble in water. As they have only a very slight alkaline taste, they may be employed for preserving food without communicating any taste to it.

They have been used in surgical operations. A solution containing 0·61 p.c. of ammonium fluosilicate is not irritating to wounds, whilst it possesses greater antiseptic power for animal tissues than 1 part of mercuric chloride in 1000 of water, which latter is a stronger solution than that which can be generally employed for surgical purposes without producing poisonous effects (Chem. News, 56, 132) (*v.* DISINFECTANTS).

A solution of free hydrofluosilicic acid

containing 26 p.c. of the acid, has been placed on the market under the name 'Keramyl' (Prior, J. Soc. Chem. Ind. 1909, 904).

FLUORINDINES *v.* AZINES.

FLUOROFORM. A gas at ordinary temperatures, said to be obtained by heating a mixture of iodoform and silver fluoride (Valentiner and Schwarz).

FLUOR-SPAR, *Fluor,* or *Fluorite.* (Ger. *Flussspat*; Fr. *Fluorine.*) A common mineral composed of calcium fluoride (CaF_2), crystallising in the cubic system. It is frequently found as well-developed crystals, usually cubes, but occasionally as octahedra; interpenetrating twinned cubes are common. An important character is the possession of perfect cleavages parallel to the faces of the octahedron. Sp.gr. 3·18; hardness 4 (the mineral can be scratched with a knife). The crystals have a bright vitreous lustre, and are frequently transparent; they may be colourless or various shades of purple, green, yellow, pink, &c., the mineral displaying a very extensive range of colour. Dull cleavage masses and massive material, sometimes quite compact or earthy, are of abundant occurrence.

The cause of the colour of fluor-spar has long been a subject of discussion, and although not yet definitely determined, it may, in some cases at least, be ascribed to the presence of traces of organic matter. Some crystals undergo a change in colour when exposed to sunlight; for example, certain greens are changed to purple. Changes in colour are also effected when the crystals are exposed to the cathode rays, or to the rays emitted by radium salts. Many crystals are decolourised when heated to a temperature ranging from 220° to 300°. The heating of the mineral is usually accompanied by a bright phosphorescence (thermo-luminescence), violent decrepitation, and the liberation of water and gases (carbon dioxide, carbon monoxide, hydrogen, nitrogen, and oxygen). The water which distils off is sometimes brown, and has a strong 'empyreumatic' odour; and it is on this account, together with the fact that the mineral is decolourised at a low temperature, that the colour has been ascribed to organic matter. It must, however, be remarked that the water and gases, and possibly also any organic matter present, are contained in the fluor-spar in vast numbers of cavities, usually of microscopic dimensions, but sometimes large enough to show a moving bubble when a crystal is turned about in the hand. A remarkable phenomenon, sometimes associated with the colour of fluor-spar, is that of fluorescence; this is best displayed by certain purple or green crystals from Weardale, Co. Durham. A crystal, which by transmitted light is pinkish or greenish, exhibits when viewed in reflected light a rich plum-blue colour with a velvety softness which has the appearance of being diffused immediately beneath the surface of the crystal. This effect is destroyed when the crystals are heated to 220° or 300°.

Fluor-spar occurs under a variety of conditions: in cavities in granite rocks, in veins of tin ore, occasionally as a cementing material in sandstone, and most abundantly as an associate of lead ore in veins traversing limestone. Some of the veins in limestone, consisting almost entirely of pure massive fluor-spar, have a thickness of 20 feet. The whole of the production in England, amounting at the present time to about 40,000 tons per annum, is from north Derbyshire, and Weardale in Co. Durham, where it is obtained chiefly as a by-product in lead-mining. Formerly, when there was little or no demand for fluor-spar, this mineral was thrown out on the waste heaps; and now that the material is of value (10*s.* to 20*s.* per ton), these extensive waste heaps are being worked over. A considerable amount, some 50,000 tons per annum, is mined in the United States, principally in southern Illinois and western Kentucky. Curiously, however, a large portion of the English fluor-spar is exported to America. Smaller quantities are obtained in Bavaria, Saxony, France, and Spain.

The name fluor, from the Latin *fluo,* to flow, was used in the form *fluores lapides* by G. Agricola in 1529, and has reference to the use of this mineral as a flux in metallurgical operations. Within recent years, its application in this direction has been very considerably extended, and now large amounts are used in the manufacture of iron and steel, chiefly in the basic open-hearth process, and of ferrosilicon and ferromanganese. If not contaminated with too much silica (not over 3 or 4 p.c.), it acts better than limestone for fluxing. To some extent, fluor-spar is also used in iron and brass foundry-work, as it produces a greater fluidity in the metal. Other applications are in the glass and enamelling industries, and in the manufacture of opaline glass. In the form of sand, the mineral is used as a binding material in emery-wheels, and for mixing with mortar and cement. Owing to its low refractive index ($\mu_D = 1{\cdot}43385$) and weak dispersion, clear and colourless fluor-spar is used with glass for the construction of the apochromatic lenses of microscope objectives, but material which is perfectly isotropic and sufficiently transparent and free from colour is difficult to obtain. A special variety of fluor-spar, known as 'blue-john,' for which the Tray Cliff cavern near Castleton in Derbyshire has long been famous, has been much used for fashioning vases and other small ornamental objects. Although occasionally used as a gem-stone on account of the delicate colouring, the mineral is much too soft for this purpose. Beads of fluor-spar have been found amongst prehistoric remains in North and South America.

Being the only common mineral containing fluorine in large amount (F 48·9 p.c.), fluor-spar is used for the preparation of hydrofluoric acid and other fluorine compounds. It is slightly soluble in hydrochloric acid and in solutions of alkali carbonates, and is readily decomposed by sulphuric acid even in the cold (on this depends its use for etching glass, a process in use long before the discovery of the element fluorine). Being almost the only substance not attacked by free fluorine, it was used by H. Moissan in the construction of his apparatus for the isolation of this element.

(On the fluor-spar deposits of Derbyshire, *see* C. B. Wedd and G. C. Drabble, Trans. Inst. Mining Eng. 1908, vol. 35, 501; on those of Weardale, *see* W. M. Egglestone, *tom. cit.* 236; on American deposits, *see* H. F. Bain

(1905), E. O. Ulrich and W. S. T. Smith (1905) in the publications of the U.S. Geological Survey. On the fluorescence, thermo-luminescence, and liquid and gaseous enclosures, *see* H. W. Morse, Proc. Amer. Acad. Sci. and Arts, 1906, vol. 41, p. 585.) L. J. S.

FLUX. A term applied in metallurgy to the material which is added to a charge of ore for the purposes of combining with earthy or metallic impurities and removing them as slag, or to any substance which is fluid at a high temperature and protects the regulus from oxidation.

All ores contain gangue, either of an acidic (silicious) or of a basic character, which, if the ore were subjected to the action of a reducing agent alone, would retain a large proportion of the reduced metal and also foul the furnace. In order to remove the gangue and the accumulated impurities from the reduced metal, it is necessary to add materials which will combine with them to form a fusible slag.

A distinction may be made between the fluxes which are used for assaying and those which are used for smelting on a large sacle, though even among the latter there are many special fluxes, *e.g.* antimony glass (*v.* ANTIMONY), for details concerning which the articles on the extraction of the several metals should be consulted.

The more important fluxes used in assaying are:

Sodium carbonate (or potassium carbonate, or a mixture of the two), which gives very fluid slags with acidic ores, and acts also as desulphurising agent.

Borax fluxes with basic materials, forming readily fusible borates of the metals. Borax has a marked influence in increasing the fluidity of most slags.

Fluorspar, used especially with phosphates, is a 'neutral' flux.

Litharge and **Red lead** are useful fluxes for oxides of iron or copper, &c.

Potassium cyanide, which acts chiefly as a reducing agent, being converted into cyanate. (For further details, *see* art. ASSAYING.)

The fluxes used on the large scale are few in number, as it is essential to the economic success of a process that the cost of slag-producing materials should be as low as possible. An economy is frequently effected by mixing together in proper proportions an ore in which the gangue is silicious in character with another containing basic impurities. In general, the character of the fluxes to be used must be decided by the nature of the ore, the object usually being so to arrange matters that the furnace charge shall contain basic and silicious constituents in the proportions required to form a fusible double silicate containing two bases. The proportion of silica present should be sufficient to combine with all the basic oxides except that which it is desired to reduce.

Fluxes are of three classes:

(1) **Acidic.** *Silica*, as quartz, sand, &c. *Natural silicates. Silicious slags.*

(2) **Basic.** *Lime* or *limestone* is the most important, being used in enormous quantities in iron smelting.

Dolomite or *magnesia* are useful also, but are more expensive.

Clay, clay-slate, &c., are largely used when the introduction of alumina is desirable.

(3) **Neutral.** *Fluor-spar.* This should be free from copper pyrites, blend, and galena, and, if possible, from quartz. Derbyshire spar is the best. It fluxes sulphates of calcium, lead, barium, calcium phosphate, silica, silicates, &c., with formation of a very fusible slag.

Roberts Austen (Metallurgy, 294) gives the following rules for the selection of fluxes to form a fusible silicate slag:—

If the gangue is silicious, two bases must be added, *e.g.* clay slate or argillaceous limestone.

If the gangue is argillaceous, the addition of one base, *e.g.* limestone, will suffice.

When the gangue is basic and contains two metallic oxides, the addition of quartz only is necessary, but when it contains only one base, clay, silicious slag, &c., must be added.

FORCITE *v.* EXPLOSIVES.

FORDIT. An explosive consisting of nitroglycerin (24·5), collodion cotton (1·0), nitrotoluene (34·0), flour (2·0), dextrin (2·0), glycerol (5·5), ammonium nitrate (32·0), and potassium chloride (30·0 parts).

FORMAL *v.* SYNTHETIC DRUGS.

FORMALDEHYDE (*formic aldehyde, formol, methanal*) CH_2O. Discovered in 1867 by A. W. Hofmann as a product of the flameless combustion of methyl alcohol. A red-hot coil of platinum wire suspended over methyl alcohol contained in a beaker, is kept red-hot so long as it is in contact with the mixture of air and methyl alcohol vapour, acting as a contact body for the formation of the formaldehyde

$$CH_3OH+O=CH_2O+H_2O.$$

Hofmann succeeded in isolating a small quantity of formaldehyde by passing the mixture of methyl alcohol vapour and air through a platinum tube heated to dull redness. Armand Gautier passed the methyl alcohol vapours through a horizontal tube heated in a sulphur bath.

Methods for preparing formaldehyde in larger quantities were devised by Tollens, Loew, and Kablukow. Air was bubbled through methyl alcohol at 40° to 50°, and the mixture of air and alcohol vapours passed over a spool of copper wire gauze 5 cm. long and moderately heated. The product was collected as an aqueous solution in a flask on a water-bath, and the gases and uncondensed vapours passed on to a receiver cooled by ice or water. Tollens found that the yield depended largely on the temperature of the methyl alcohol, and therefore on the degree of saturation of the air with alcohol:

Temp. of bath	Yield of CH_2O
22°–32°	17·95
38°–44°	28·90
45°–50°	31·15

Trillat proposed the first method for the production of formaldehyde on a manufacturing scale (Fr. Pat. 199919, 1889; D. R. P. 55176). His apparatus is shown in Fig. 1. Crude or rectified methyl alcohol is heated in the copper vessel A of about 100 litres capacity by passing steam through the bottom compartment *a*. The alcohol vapours are carried away by the copper pipe B fitted with a conical perforated mouthpiece C, and issue from the perforations in

form of a fine spray. The mouthpiece penetrates a short distance into tube D of 10 cm. diameter and 1 m. length. Air can be aspirated through x at the conical end of D as indicated by the arrows.

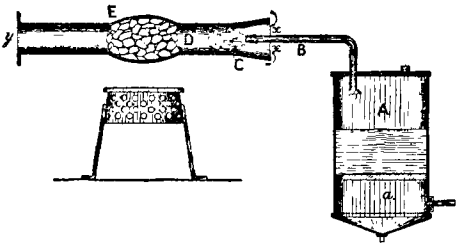


FIG. 1.

Platinised asbestos is placed in the widened part at E and heated by direct fire. Other contact substances which were suggested by Trillat are copper oxide, retort carbon, porcelain, coke, firebrick, and the like. The method of working is as follows :—

The tube was heated at E to a dull or bright red heat, according to the nature of the contact substance; the receiver, communicating with a vacuum pump, is then connected to y. The methyl alcohol was in the mean time brought to boiling-point; and the vapours produced, forming a spray, were mixed with air drawn in at x. The mixture reacts on meeting contact substance, whereby the alcohol is then oxidised to formaldehyde. The vapours contain water, undecomposed methyl alcohol, and traces of formic and acetic acids. The products are condensed or dissolved in water, and the solution redistilled to drive off the impurities. Trillat gave no statements of yields, but these cannot have been very good, and his apparatus is therefore to-day only of historic interest. It formed, however, the basis for the present processes. Instead of boiling the alcohol and subsequently mixing its vapours with air, later processes drive or draw air through the methyl alcohol, kept at a temperature suitable for saturation, and pass the mixture over the contact substances.

M. Klar and C. Schulze proposed the introduction of the scrubber principle for this operation (D. R. P. 106495). They consider the large excess of alcohol over air obtained by the older method to be disadvantageous, and otherwise undesirable. At the same time, there is too little control over the ratio of the mixture. They therefore employ a scrubber, made of metal or stoneware, into which they pass a fine spray of wood spirit through a rose. Air, which has previously been heated high enough to obtain a mixture temperature of 45°–50°, is blown in at the bottom of the scrubber which may also be provided with a steam-jacket. By adjusting the flow of alcohol and air, the ratio of the mixture can be varied to any desired extent. In order further to moderate the oxidation, the air is diluted with a certain proportion of nitrogen obtained from the process itself, with the result that a smaller degree of saturation of the air is required. They claim advantages both in regard to the safety and the yield of their process. This process relates only to the preparation of the reacting mixture, but has no reference to the contact process proper.

Fig. 2 shows the formaldehyde plant of a

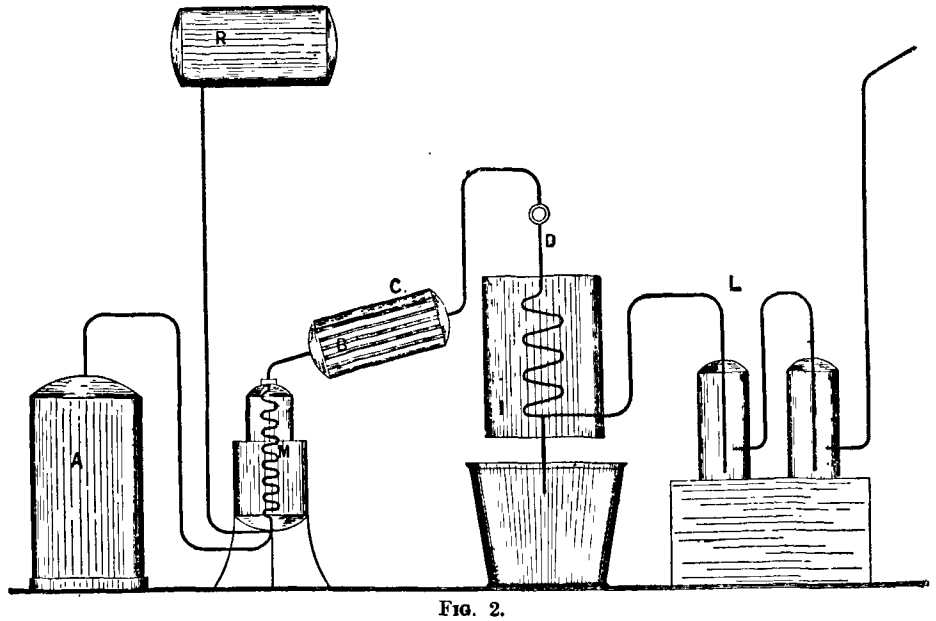


FIG. 2.

French factory (Côte d'Or), as described by A. Morel (J. Pharm. Chim. 1905, 21, 177). The principal unit is the oxidiser, a metal cylinder C, fitted with copper tubes B in which the reaction takes place. Wood spirit is supplied from the tank R to the mixer M, constructed on the carburettor principle, and is here vapourised by, and in suitable proportions mixed with, air pressed in from reservoir A. The mixture reacts during its passage over copper contacts placed in

the oxidiser tubes D kept at an elevated temperature. Sight holes permit of the observation of colour and luminosity, and consequently the temperature of the contact zone. The products are carried off through a single pipe, and are condensed in coil D surrounded by a current of water. The condensate, being crude formaldehyde solution, runs into a receiver. The uncondensed vapour is extracted from the gases in three washers, L. The crude product is freed from methyl alcohol in a rectifying still.

The modern plants for the manufacture of formaldehyde are built on the same lines, although greatly improved in some of the details, with the result of a greatly increased yield. In Fig. 3 a modern plant is shown. Compressor 1 aspirates air from the atmosphere and presses it into the air vessel 2, in which a constant pressure is kept. Methyl alcohol runs from tank 3 into the carburation vessel 4. A heating arrangement is placed in this apparatus which raises the temperature of the incoming air. This current of air meets a thin stream of methyl alcohol, which also takes up heat, and a mixture of constant composition is thereby formed. This enters the oxidiser 5, charged with the contact substance, which usually consists of copper gauze, but in some cases silver or silver-coated copper gauze is used in preference. The products of reaction issuing from the oxidiser, which consist of vapours of formaldehyde, water, and the excess of methyl alcohol, as well as nitrogen and hydrogen, pass into a separator, 6, in which, by a washing process, commercial formaldehyde (40 p.c. solution)—so-called 'formalin'—is obtained, which is drawn off into the receiver 8, whilst methyl alcohol vapours are almost completely condensed in 7, whence they run into reservoir 12, and are sent by pump 13 back into the feeding tank 3. The gases still contain some methyl alcohol, and are made to pass the washer 9 which extracts the last traces. This dilute alcohol is concentrated in the continuously working rectifying still 10. The concentrated alcohol vapours are again condensed in 11, and pumped back to 3.

J. E. Orloff has devised a further modification of the formaldehyde plant. In order to

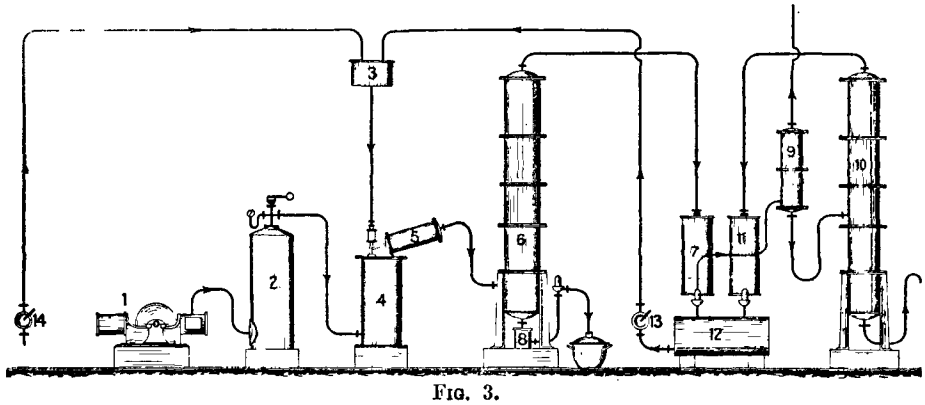


FIG. 3.

start the work of the oxidiser without the application of external heat, he employs 'ignition pills,' made of platinised asbestos or pumice, close to the contact bodies, which initiate the reaction at ordinary temperature when the alcohol vapours pass over them. It is found that an alcohol vapour of 90 p.c. strength gives satisfactory results; this makes it possible to distil the alcohol completely without a rectifying column, whilst, when working with vapour of 100 p.c. strength, the alcohol has to be rectified after one quarter is distilled off. The dephlegmator is kept at 53°–54°, whilst it showed 42°–43° only when external leading was applied. Orloff's oxidiser consists of 169 copper tubes of 19 mm. internal diameter, 2 mm. thickness, and 800 mm. length, arranged in seven concentric circles between two plates of 820 mm. diameter, which are separated from the two cover plates by bronze rings of 720 mm. int. diam. A steam coil is placed in the ring on the inlet side to heat the mixture, which enters through a pipe 50 mm. wide. A number of sight holes are provided in the front plate, and a conical exit pipe is connected with the back ring. Glass tubes, 16 mm. wide, 1·25 mm. thick and 300 mm. long, are placed in the copper tubes containing spools 120 mm. long, made of copper gauze. The air drawn through the system by a vacuum pump is measured in a gas meter. The methyl alcohol should be of 90 p.c. strength, and contain not more than 1 p.c. acetone. The ratio of the volume of exit gases to the volume of air admitted should be 1·15 : 1 on an average. An apparatus of the size given oxidises 175 kgs. methyl alcohol in 10 hours, and the yield should be 150 to 155 p.c. by weight of the alcohol employed, the formaldehyde having a strength of 38–39 p.c.

The bulk of the world's production of formaldehyde is made from methyl alcohol. There have, however, been various proposals for the employment of other raw products. Glock (D. R. P. 109014) suggests the oxidation of methane, or mixtures containing methane, by oxygen in presence of copper, pumice, or asbestos as a catalyser. Methane is mixed with an equal volume of air and passed through a tube filled with granulated copper heated to 600°. The products are cooled, washed with water, mixed with an equal volume of air, and again passed through a second tube with contact substance and this process is repeated until all methane is oxidised. The first tube is kept hot by the reaction, the others require external

heating. Hydrogen peroxide, or, according to Lange and Elworthy's Fr. Pat. 352687, electrolytically produced persulphuric acid, have been suggested as oxidising agents in the production of formaldehyde from alcohol.

Theory of the contact process. After the early work of Hofmann, Tollens, Loew, Kablukow, the subject was closely investigated by Trillat, who published these researches in his book 'Oxydation des Alcools par l'action de contact.'

He studied the influence of varying temperatures, proportion of air and of water, and of different contact substances, on the oxidation process. His conclusions were partly incorrect, particularly with regard to the proportion of water vapour to methyl alcohol, which he, in contradistinction to other investigators, did not consider injurious.

J. E. Orloff, in a series of papers in the Journal of the Russian Chemical Society, assumed the main reaction to be:

$$2CH_3OH+O_2=2CH_2O+2H_2O$$

with a secondary oxidation to formic acid and carbon dioxide, and carbon monoxide and water. No traces of formic acid could, however, be found, but always hydrogen, and he therefore suggested a partial decomposition:

$$CH_2O=CO+H_2$$
$$CO+O=CO_2$$
$$H_2+O=H_2O$$

The main reaction is not in accordance with the facts established by Ipatieff and by Sabatier and Senderens, who had proved the catalytic decomposition of alcohols into aldehydes and hydrogen generally, with copper as catalyst. M. Le Blanc and E. Plaschke (Zeitsch. Elektrochem. 1911, 17, 45) have established that the formation of formaldehyde is due not to oxidation, but to catalytic dehydrogenation of methyl alcohol. The activity of freshly reduced copper or silver decreases rapidly unless air is introduced with consequent temporary oxidation of the metal. This is again reduced at the expense of alcohol and possibly aldehyde. An undesirable secondary reaction is the decomposition of formaldehyde into hydrogen and carbon monoxide. The yield is dependent upon the temperature of the contact body, the ratio of alcohol to air or oxygen, and the surface of the contact body. The highest yield was 58 p.c., and the lowest loss of destroyed alcohol 12 p.c.

Formaldehyde is a gas of characteristic smell which, on cooling, condenses to a liquid of b.p. −21° and of sp.gr. 0·8153 at −20° or 0·9172 at −80°. Liquid formaldehyde changes at −20° readily into a solid modification; the melting-point of monomolecular CH_2O is −92°. Water absorbs up to 52 p.c. formaldehyde; the freshly prepared concentrated solution, which has a pungent smell, contains diformaldehyde or methyleneglycol $CH_2(OH)_2$, which changes into formaldehyde on standing. Dilute solutions contain the monomolecular form CH_2O, and do not undergo any change when kept in closed vessels. But on concentrating the solution in a desiccator or by evaporation, polymerisation takes place, flocculent masses of $(CH_2O)_nH_2O$ ($n=6$ to 8) being precipitated, which form the commercial paraformaldehyde.

The aqueous solution precipitates from an ammoniacal silver solution a specular deposit of silver, and, on treatment with sulphuretted hydrogen, yields crystals of trithiomethylene $(CH_2S)_3$ (Hofmann, Annalen, 145, 360). On heating formaldehyde with a dilute solution of sodium hydroxide, formic acid and methyl alcohol are produced. With concentrated sodium hydroxide solution and a little Cu_2O, formic acid is produced at ordinary temperature, accompanied by violent evolution of hydrogen (Loew). Formaldehyde readily combines with ammonia to form the monacid base *hexamethylenetetramine*, according to the equation:

$$6CH_2O+4NH_3=N_4(CH_2)_6+6H_2O.$$

As this reaction takes place even in dilute solution, it forms a convenient method for the titrimetric determination of formaldehyde (Butlerow, Annalen, 115, 322; Legler, Ber. 16, 1333; Loew, J. pr. Chem. 1886, 33, 326). It crystallises from alcohol in rhombohedra, is very soluble in water and alcohol, and insoluble in ether.

Formaldehyde condenses with aniline with loss of water to *anhydroformaldehydeaniline*

$$CH_2O+C_6H_5NH_2=C_6H_5N:CH_2+H_2O.$$

On heating formaldehyde with a solution of ammonium sulphate, *trimethylamine sulphate* is formed, whereby one-third is oxidised to CO_2 (Plöchl, Ber. 21, 2117). $CH_2O,NaHSO_3,H_2O$ is formed by adding $NaHSO_3$ and alcohol to formaldehyde solution; this is readily soluble in water and methyl alcohol, less soluble in ethyl alcohol. By the action of hydrogen chloride on formaldehyde, Tischtschenko obtained *dichloromethyl ether* and water. Lösekann obtained, by the same treatment, *oxychloromethyl ether*, which further yielded *monochloromethyl alcohol* (Ber. 25, 92). By careful treatment with bases such as calcium hydroxide or lead oxide, formaldehyde may be polymerised into a mixture of saccharine substances. By continual boiling of such a solution with tin, *iso*formose is obtained; treatment with lime water yields *α-acrose* $C_6H_{12}O_6$.

If formaldehyde solution is concentrated in the presence of dehydrating agents, it polymerises to *trioxymethylene* $(CH_2O)_3$, a crystalline mass fusing at 171°–172°, but subliming below 100°; insoluble in water, alcohol, or ether at ordinary temperature, but soluble in water when heated to 130°, when it appears to be converted into formaldehyde or paraformaldehyde (Tollens and Mayer, Ber. 21, 3504). When trioxymethylene is volatilised, it dissociates completely into formaldehyde (v.d. 15·3, Hofmann). When boiled with lime water, it yields formic acid and an amorphous saccharine substance, *methylenitan* (Butlerow, Annalen, 120, 295).

When dry trioxymethylene is heated in a sealed tube with traces of sulphuric acid at 115°, it is converted into the isomeric α-trioxymethylene $(CH_2O)_3$, which crystallises in needles, melts at 60°–61°, and sublimes at ordinary temperature, and is soluble in water, alcohol, and ether (Pratesi, Gazz. chim. ital. 14, 139).

Auerbach and Barchall (Arb. Kais. Gesundh. Amt. 27, part 1) claim to have established the identity of six individual polymerides: paraformaldehyde $(CH_2O)_n+H_2O$, four polyoxymethylenes $(CH_2O)_n$ and α-trioxymethylene $(C_3H_6O_3)$ of ring structure, characterised by

their form (amorphous, colloidal, indefinite crystals, definite crystals, and well-developed crystals), melting-point, solubility, &c.

Formaldehyde is capable of reacting with practically any class of organic, and a large number of inorganic, substances, and forms numerous condensation products. It reacts with hydrocarbons, carbohydrates, aldehydes, and ketones, carboxylic, oxy- and keto- acids and their esters, phenols, oxyaldehydes, gallic and tannic acid, amines, ammonia, hydrocyanic acid, hydrazines, hydroxylamine, urea, uric acid, guanidine, the proteins, nitro compounds, quinoline, pyridine, and sulphur compounds.

Its formation plays an important part in the assimilation of carbon dioxide by chlorophyll-containing plants (Baeyer, Bach, Loeb, Delépine).

The industrial employment of formaldehyde is manifold, in keeping with its enormous reactivity. The coal-tar colour industry uses it very largely for condensation products; a great number of pharmaceutical preparations have formaldehyde as their active principle. In most of these, use is made of its antiseptic powers by condensation with a variety of drugs.

The antiseptic properties of formaldehyde are essentially due to its chemically combining with the cell skin of the micro-organisms, thereby hardening it and inhibiting their growth. It is employed in a number of ways and in different combinations. It is used in the treatment of wounds and for sterilising surgical instruments and the hands of operators, occasionally compounded with soap, as in *lysoform*. For disinfecting rooms a 1 or 2 p.c. solution of formaldehyde may be used as spray, and is non-injurious to coloured fabrics. A concentrated solution or solid paraformaldehyde may be vapourised in a lamp, and its diffusive and penetrating qualities make it applicable where other disinfectants cannot be employed. The best known forms of apparatus for this purpose were devised by Trillat, Tollens, Krell, Barthel, and Schering. In certain cases, as for instance in the treatment of frozen meat on board ship, an air current is passed through a vessel containing formaldehyde solution heated by steam coils. It has also been proposed to treat a mixture of paraformaldehyde and peroxides of the alkaline earths with water, when a violent liberation of formaldehyde vapour takes place (Autan).

Its preservative qualities are made use of in embalming and for the preservation of corpses for dissection. It is largely used for the preserving of foodstuffs, and possibly the effect of 'curing' is in a measure due to the formaldehyde produced from burning wood and other carbonaceous materials.

Formaldehyde is employed in the brewing, distilling, and sugar industries, and besides its preservative action, a certain stimulative effect on the diastatic properties of the malt, and on the activity of yeast, has been observed. Formaldehyde is largely used for tanning purposes, especially for sole leather. By its action on proteid bodies, it makes the leather hard and firm without having the bad effect of acids. In the paper-making and textile industries, it is used for fixing glues and sizes, and also for water-proofing fabrics, by rendering gelatin or casein insoluble. Upon the same reaction is based its employment in hardening the gelatin films of photographic plates, and for hardening microscopic preparations and anatomical museum specimens.

Formaldehyde is also used as a reducing agent in the recovery of silver and gold, and in the preparation of metallic mirrors. A material for the manufacture of bone-like articles is made by the action of formaldehyde on caseinogenate (galalith), and on the condensing reaction of formaldehyde with phenol or cresols is based the manufacture of a substitute for horn, tortoiseshell, &c. (bakelite).

For the qualitative detection of formaldehyde, a number of reactions have been proposed, most of which are based on colour reactions. On warming with ammoniacal silver solution, the silver mirror is produced. Schiff's reagent is frequently used; 0·4 gram magenta is dissolved in 25 c.c. of water; 10 c.c. of sodium bisulphite solution (sp.gr. 1·375), and then 10 c.c. of strong sulphuric acid are added; formaldehyde causes a red colouration which, on addition of hydrochloric acid, changes to bluish violet. Other reagents suggested are alkaline resorcinol, phloroglucin, codeine, morphine, phenyl hydrazine, and ferric chloride.

For the quantitative determination, the following are used: Legler's method based on the reaction of ammonia on formaldehyde, gives low results. For impure concentrated solution, the method of Blank and Finkenbeiner (Ber. 31, 2979) may be employed. It consists in oxidising formaldehyde to formic acid by means of hydrogen peroxide in alkaline solution. An iodometric method was suggested by Romijn (Zeitsch. anal. Chem. 36, 19), and many colorimetric reactions have been worked out for the exact estimation of small quantities of formaldehyde. 1 part of formalin in 100,000 parts of milk can be detected by distillation and application of colour reactions to the distillate. Rideal and Hehner have studied the rate of disappearance of formalin when added to milk by formation of condensation products. Schryver uses phenyl hydrazine and potassium ferricyanide for the estimation of formaldehyde in a dilution of 1 : 1,000,000. R. L.

FORMALIN. A 40 p.c. solution of formaldehyde.

FORMAMIDE $HCO{\cdot}NH_2$. First obtained by Hofmann (J. pr. Chem. 91, 61) by heating ethyl formate with ammonia in a sealed tube at 100°.

It is a product of the oxidation of amino-acids, lactic acid, albumin, &c., by ammoniacal potassium permanganate (Hasley, Zeitsch. physiol. Chem. 25, 325).

It is formed by the action of the silent discharge on a mixture of carbonic oxide and ammonia (Losanitsch and Jovitschitsch, Ber. 30, 138); by distilling sodium formate with ammonium chloride in a vacuum (Verley, Bull. Soc. chim. 9, [3] 691); or by heating crystallised ammonium formate in a sealed tube at 230° for 5 hours (Hofmann, Ber. 15, 980), but is best prepared by heating pure dry ammonium formate for 2 hours at 100°–180° in an atmosphere of ammonia, then fractionating in the same atmosphere at ½ mm. pressure (Freer and Sherman, Amer. Chem. J. 20, 223).

Formamide is a liquid, b.p. 85°–95° (½ mm. pressure); at ordinary pressure it decomposes, when heated above 100°, into carbon monoxide, ammonia, hydrogen cyanide, and water. At 1° it crystallises in needles; sp.gr. 1·76 at 4° (Freer and Sherman, *l.c.*). Phosphorus pentoxide converts it into water and hydrocyanic acid: $HCO{\cdot}NH_2=HCN+H_2O$. Strong caustic potash decomposes it, even in the cold, into potassium formate and ammonia. It is also decomposed by a mixture of potassium chromate and sulphuric acid, forming carbon dioxide and ammonium hydrogen sulphate; by hydrogen peroxide with production of ammonia and carbon dioxide (de Coninck, Compt. rend. 128, 503); and by sodium hypochlorite on heating (de Coninck, *ibid.* 121, 893). Formamide combines with chloral forming chloral-amid or *chloralum formamidatum*, used as a disinfectant and as a preservative, and for its hypnotic properties (*v.* CHLORAL). Sodium, silver (Freer and Sherman, Amer. Chem. J. 562 and *l.c.*; Titherley, Chem. Soc. Trans. 1897, 466) and mercury salts have been obtained (Fischer and Grützner, Arch. Pharm. 232, 329). Condensation products of value as antiseptics and solvents for uric acid are obtained by condensing formamide with formaldehyde, paraldehyde, or trioxymethylene (J. Soc. Chem. Ind. 25, 283).

FORMAMIDINE, *Methenylamidine*

$CH(NH)(NH_2)$.

This compound, the lowest member of the amidine series, may be regarded as formamide $HCO{\cdot}NH_2$ in which the oxygen atom has been replaced by imidogen. Obtained by acting on the double compound of hydrocyanic acid and hydrochloric acid with absolute alcohol:

$2HCN,HCl+2C_2H_5{\cdot}OH$
$=CH(NH)(NH_2),HCl+C_2H_5Cl+HCO_2{\cdot}C_2H_5$

(Gautier, Compt. rend. 65, 410; *cf.* Claisen and Matthews, Chem. Soc. Trans. 1882, 265). From the hydrochloride of formimido-ether

$CH(NH)(OC_2H_5),HCl$

and alcoholic ammonia (Pinner, Ber. 16, 375, 1647). Formamidine hydrochloride crystallises from alcohol in hygroscopic granules, melting at 81°, and decomposing at 100° into hydrocyanic acid and ammonium chloride:

$CH(NH)(NH_2)HCl=HCN+NH_4Cl$.

When liberated from its salts by caustic potash, formamidine is at once decomposed into ammonia and potassium formate. Its salts crystallise with difficulty. $(CH_4N_2,HCl)_2,PtCl_4$ forms very soluble, orange-red, quadratic pyramids.

Formamidine picrate

$NH:CH{\cdot}NH_2,C_6H_2(NO_2)_3OH$,

obtained by the addition of formamidine hydrochloride to picric acid, crystallises in long lustrous yellow needles, m.p. 248° (Diechmann, Ber. 25, 705).

Substitution derivatives of formamidine have been studied by Dains (*ibid.* 35, 2496).

FORMAN. Trade name for chlormethylmenthyl ether $C_{10}H_{19}{\cdot}O{\cdot}CH_2Cl$, formed by the action of formaldehyde upon menthol in the presence of hydrochloric acid. A colourless, fuming oil, b.p. 160°–162°, 16 mm. pressure, decomposed by water into its original constituents. Employed in medicine in catarrhous affections of the air passages (*v.* SYNTHETIC DRUGS).

FORMANILIDE $HCO{\cdot}NH{\cdot}C_6H_5$, or

$OH{\cdot}CH:N{\cdot}C_6H_5$

(Claisen, Annalen, 287, 360; Wheeler and Medcalfe, Amer. Chem. J. 19, 217). First obtained by Gerhardt (Annalen, 60, 310) by heating aniline oxalate. Best prepared by heating together molecular proportions of aniline and strong formic acid on the water-bath under reduced pressure to remove the water, then distilling under ordinary pressure until the thermometer indicates 250°, and finally pouring out the undistilled portion, when it solidifies on standing (Wallach and Wüsten, Ber. 16, 145).—Long four-sided prisms melting at 46°, moderately soluble in water, readily so in alcohol. Dilute acids decompose it into aniline and formic acid. Formanilide is rapidly attacked by chromic acid, various colouring matters being formed (de Coninck, Compt. rend. 128, 503).

Sodium, silver (Comstock, Ber. 23, 2274; Comstock and Kleeberg, Amer. Chem. J. 12, 493), and mercury compounds have been obtained (Wheeler and McFarland, *ibid.* 18, 540).

Other derivatives are described by Comstock and Kleeberg (*l.c.*), Claisen (*l.c.*), and Komstock and Wheeler (Amer. Chem. J. 13, 514).

FORMIC ACID (Ger. *Ameisensaure*) $H{\cdot}COOH$. Discovered by Rey, in 1670, by distilling red ants with water. Formed in the acid secretions of certain caterpillars; in the common nettle; in the fruit of the soap-nut tree (*Sapindus saponaria* (Linn.)); in tamarinds, &c. Occurs in sweat, urine, and muscular plasma. Formed by the dry distillation of starch, sugar, gum, tartaric and oxalic acids, &c. Best obtained by heating a mixture of glycerol (or other polyatomic alcohol of high boiling-point) with crystallised oxalic acid. The anhydrous glycerol is heated with the oxalic acid to 75°–90° until the evolution of carbon dioxide ceases, when a fresh quantity of oxalic acid is added, and the process repeated. The oxalic acid $C_2H_2O_4{\cdot}2H_2O$ decomposes into water, carbon dioxide, and formic acid, which reacts upon the glycerol, forming *monoformin*.

On the addition of a further quantity of crystallised oxalic acid, the water of crystallisation decomposes the monoformin, producing glycerol and formic acid, which distils over

$C_3H_5(OH)_3+H{\cdot}COOH=HCO{\cdot}OC_3H_5(OH)_2+H_2O$

Glycerol. Formic acid. Monoformin.

monoformin is thus being continually formed and destroyed, with the eventual production of formic acid of from 87 to 88 p.c. (Lorin, Bull. Soc. chim. [*ii.*] 5, 7; 20, 241; 24, 22 and 436).

Formic acid is also obtained by heating formates *in vacuó* with acids or acid salts (Hempel, Eng. Pat. 3428; J. Soc. Chem. Ind. 1909, 259); by treating formates with hydrofluoric acid (Strauss, D. R. P. 209418; J. Soc. Chem. Ind. 1909, 674); and by heating in a still 1 part of sodium formate with 2 parts of sodium hydrogen sulphate or other acid salt; in the last method, acid of from 97 to 98 p.c. is obtained (Ch. Fab. Grünaw, Landshoff, und Meyer, Akt. Ges., Eng. Pat. 14438; D. R. P. 192881; Fr. Pat. 367316; U.S. Pat. 857046; *v.* also Hamel, Eng. Pat. 7534; Fr. Pat. 341764; U.S. Pat. 806660; J. Soc. Chem. Ind. 1904, 9113, and Soc.

Anon. des Etab. Eycken and Leroy; Fr. Pat. 393526; J. Soc. Chem. Ind. 1909, 160).

Anhydrous formic acid may be obtained by gently heating lead formate with sulphuretted hydrogen, or by heating the dehydrated sodium salt with anhydrous oxalic acid. It is a colourless, slightly fuming liquid, with a penetrating smell, and is intensely corrosive. Boils at 99·9°, sp.gr. 1·2211, solidifies at a low temperature, forming large brilliant plates; m.p. 8·6°. Traces of water lower the m.p. and raise the b.p. The specific gravity of aqueous solutions is given in the following table (Richardson and Allaire, Amer. Chem. J. 19, 150):—

P.c.	Sp.gr. 20°/4°	P.c.	Sp.gr. 20°/4°
10	1·0247	60	1·1425
20	1·0489	70	1·1656
30	1·0730	80	1·1861
40	1·0964	90	1·2045
50	1·1208	—	—

Heated with concentrated sulphuric acid, formates evolve carbon monoxide: with ferric chloride neutral solutions give a red colour. Silver nitrate is reduced to metallic silver, which is precipitated, partly as a black powder, and partly as a lustrous deposit on the tube. Mercuric chloride is reduced to mercurous chloride, and if excess of formic acid is present, to metallic mercury.

Formic acid may be estimated by the method of Jones (Amer. Chem. J. 17, 539). The solution is made alkaline with sodium carbonate, warmed, and an excess of standard permanganate added. The solution is acidified, and a measured volume of oxalic acid is run in, until the precipitate of manganese hydroxide has dissolved and the permanganate disappeared. The excess of oxalic acid is estimated by titration with standard permanganate. A volume of oxalic acid, equal to that taken is also titrated with permanganate solution, and the difference between the result and the total permanganate used gives the quantity of permanganate required to oxidise the formic acid (*v.* also Rupp, Zeitsch. anal. Chem. 1906, 687; Grossmann and Aufrecht, Ber. 1906, 2455). Other methods depend on the reduction of mercuric chloride to mercurous chloride (Scala, J. anal. and appl. Chem. 5, 233; Lieben, Monatsh. 1893, 746; Leys, Mon. Sci. 12, 632; Franzen and Greve, J. pr. Chem. 1909, 80, 368); the titration of the acid with standard alkali, or the decomposition of the acid in the carbonic acid apparatus with sulphuric acid and potassium dichromate (Rupp, Arch. Pharm. 243, 69). For estimation in the presence of acetic acid, *v.* Freyer, Chem. Zeit. 1895, 1184.

Formic acid is a strong reducing agent and a powerful antiseptic. It is used as a food preservative (Woodman and Burrell, Tech. Quart. 1908, 21, 1), and in brewing is added to the yeast mash as an antiseptic (Lange, J. Soc. Chem. Ind. 1905, 1025; Henneberg, *ibid.* 1906, 192). It is used in dyeing as an assistant or reducing agent with potassium dichromate mordant and also for dyeing woollen goods or unions with acid dyestuffs (Kapff, *ibid.* 1905, 129; Meltner, *ibid.* 435; and Ruby, *ibid.* 1907, 467).

Salts and esters. Many methods for producing the salts of formic acid have been patented. In the majority of them, carbon monoxide under pressure is passed over metallic oxides, basic minerals, or alkali hydroxides, the conditions varying slightly in the different methods (Usines des Moulins, Fr. Pat. 382001; J. Soc. Chem. Ind. 1908, 183; Ellis, U.S. Pat. 875055, *ibid.*; Raschen, J. Soc. Chem. Ind. 1908, 420; Eng. Pat. 13953; Farb. Meister, Lucius and Bruning, Fr. Pat. 389065; J. Soc. Chem. Ind. 1908, 769; Haase, Eng. Pat. 4771; J. Soc. Chem. Ind. 1908, 898; Elect. Werke, D. R. P. 179515; Chem. Soc. Abstr. 1907, i. 378; Koepp and Co. D. R. P. 209417; Fr. Pat. 342168; Chem. Zentr. 1909, i. 1785). Rogatien (Eng. Pat. 12604; J. Soc. Chem. Ind. 1893, 864) obtains a mixture of ammonium formate and bicarbonate by passing moist nitrogen, hydrogen, and carbon dioxide over slightly heated pumice or other absorbent bodies. Water gas and 'Ebelmen gas' are used to supply the hydrogen and nitrogen respectively. Another method consists in treating the cyanides of the alkaline earth metals with water vapour under pressure below 300°, whereby ammonia and a formate are produced (Bad. Anil. und Soda Fab., Eng. Pat. 22038; Fr. Pat. 372714; J. Soc. Chem. Ind. 1907, 527).

Potassium formate CHO_2K and *Sodium formate* CHO_2Na are readily soluble deliquescent salts which, according to Bineau, form acid salts on solution in hot concentrated formic acid. *Calcium formate* $(CHO_2)_2Ca$ and *Barium formate* $(CHO_2)_2Ba$ crystallise in rhombic prisms, readily soluble in water, insoluble in alcohol. *Lead formate* $(CHO_2)_2Pb$ is less soluble in water than other formates, 1 part dissolving in 63 parts of water at 16°, and is insoluble in alcohol; the solution forms a series of basic formates on being warmed with lead oxide, which have an alkaline reaction and crystallise in needles. *Copper formate* $(CHO_2)_2Cu,4H_2O$ crystallises in light blue monoclinic prisms: forms a basic salt $Cu(CHO_2)_2{\cdot}Cu(OH)_2$ (Riban, Bull. Soc. chim. 38, 112). Silver and mercurous formates decompose even in the dark, and the latter deflagrates when heated and decomposes on percussion. *Methyl formate* boils at 30·4° (712 mm.), sp.gr. 0·9928: it is best made by acting on dry sodium formate with a mixture of methyl alcohol and aqueous hydrochloric acid, or by digesting methyl alcohol with concentrated formic acid. *Ethyl formate* boils at 50·4°, and has sp.gr. 0·9445 at 0°. It is made by heating a mixture of 6 parts of alcohol (90 p.c.), 7 parts of sodium formate, and 10 parts of concentrated sulphuric acid.

FORMICIN, FORMIDIN *v.* SYNTHETIC DRUGS.

FORMINS are esters produced by the condensation of glycerol or other polyhydric alcohol with formic acid.

Monoformin $HCO{\cdot}OC_3H_5(OH)_2$ is produced in the preparation of formic acid by heating glycerol with oxalic acid at 190° (Tollens and Henninger, Bull. Soc. chim. [ii.] 11, 395), and is extracted from the mixed product by means of ether. It is also prepared by the interaction of monochlorhydrin and sodium formate at 160° (van Romburgh, Rec. trav. chim. 1, 186). On distillation under atmospheric pressure it decomposes into carbon dioxide, water and allyl alcohol, but may be distilled unchanged *in vacuo*.

Dinitroformin is a yellow oil, sp.gr. 1·5 at 15°. It is formed together with nitroglycerin by heating anhydrous oxalic acid with glycerol at 150° and treating the product with nitrosulphuric acid (Vender, D. R. P. 209943; Chem. Soc. Abstr. 1909, i. 692).

Diformin $(HCO{\cdot}O)_2C_3H_5{\cdot}OH$ is the chief constituent of the residue obtained in the preparation of formic acid by heating anhydrous oxalic acid and glycerol at 140° (van Romburgh, J. 1881, 508). It is extracted with ether and purified by distillation under reduced pressure. B.p. 163°–166° under 20–30 mm.; sp.gr. 1·304 at 15°. Insoluble in carbon disulphide and decomposed by water with the formation of glycerol and formic acid. On heating under atmospheric pressure it is decomposed into carbon dioxide, water and allyl formate. With 5 parts of glycerol at 220°, carbon monoxide, carbon dioxide and allyl alcohol are the products, whilst with oxalic acid, carbon dioxide and formic acid are produced.

Triformin $(HCO{\cdot}O)_3C_3H_5$ is prepared by heating glycerol with excess of 100 p.c. formic acid. By cooling the viscous product by liquid ammonia, a crystalline mass is obtained. Pure triformin is colourless; has m.p. 18°; b.p. 266°/762 mm.; $n_D^{18°}=1{\cdot}4412$. It is saponified slowly by cold, readily by hot water (van Romburgh, Zeitsch. physikal. Chem. 1910, 70, 459).

By heating erythrol with formic acid and distilling off the acid at 200°, a mixture of formins is obtained, from which a tetraformin has been isolated. This forms silky needles, m.p. 150° (Henninger, Compt. rend. 98, 149).

FORMOPYRINE. A compound of antipyrine and formaldehyde $C_{11}H_{13}ON_2{\cdot}CH_2O$; m.p. 142°; insoluble in cold water, soluble in chloroform and alcohol. Forms salts with acids (Marcourt, Bull. Soc. chim. 1896, 520). Stolz (Ber. 1896, 29, 1826) and Pellizzari (Gazz. chim. ital. 1896, 26, ii. 407) show that Marcourt's 'formopyrine' is identical with methylene diantipyrine $CH_2(C_{11}H_{12}ON_2)_2$, described by Pellizzari (Chem. Soc. Abstr. 1890, 645).

FORMOSE *v.* CARBOHYDRATES.

FOSSIL RESINS *v.* RESINS.

FRACTIONAL DISTILLATION *v.* DISTILLATION.

FRAGARIANIN *v.* TANNINS.

FRANGULIN *v.* GLUCOSIDES; also CASCARA SAGRADA.

FRANKINCENSE *v.* GUM RESINS.

FRANKLINITE. A member of the spinel group of minerals with the general formula $R''O{\cdot}R_2'''O_3$, where R″=Fe, Zn, Mn, and R‴=Fe, Mn. The actual composition is very variable: ferric oxide always predominates (56–67 p.c.), zinc oxide ranges from 6 to 23 p.c., and manganese oxides (MnO, Mn_2O_3) average 15–20 p.c. The mineral occurs as well-developed crystals of octahedral habit, as rounded grains, and as granular masses. It is black with a submetallic lustre, much resembling magnetite in appearance, but is readily distinguishable from this in being only slightly magnetic. Sp.gr. 5·0–5·2; hardness, 6.

Although known only from Franklin in New Jersey (hence the name), it is found there in considerable abundance in association with ores of zinc in crystalline limestone. After the extraction of the zinc, the residue is used in the manufacture of spiegeleisen. L. J. S.

FRAXETIN *v.* HORSE CHESTNUT.

FRAXIN *v.* GLUCOSIDES; also HORSE CHESTNUT.

FRAXITANNIC ACID *v.* TANNINS.

FREESTONE. A rock which admits of being freely worked in any direction for use as a building stone. Many stratified rocks may be readily sawn when freshly quarried, and while holding the 'quarry-water,' but acquire considerable hardness on exposure to the atmosphere. Most freestones are either limestones or sandstones. In the Inferior Oolite there are certain beds known to geologists as the Lower and Upper Freestones, which are largely quarried as building stones, near Cheltenham. The Bath stone from the Great Oolite, and the Portland stone from the Upper Oolites, are also well-known Oolitic freestones. Many of the Coal-measure sandstones admit of being readily cut and tooled, and, being without any marked tendency to split in definite directions, are valuable freestones; such, for instance, are the sandstones of Craigleith, near Edinburgh, and of Darley Dale in Derbyshire. F. W. R.

FREIBERGITE. An argentiferous tetrahedrite occurring typically at Freiberg in Saxony, whence the name. It is generally known to German miners as *Weissgiltigerz*. Analysis, by H. Rose, of a crystallised specimen from Freiberg, yielded 31·29 p.c. silver (*v.* FAHLORE). L. J. S.

FRENCH CHALK. A variety of steatite, or soap-stone, used for marking cloth and for removing grease from silk. It is a hydrated magnesium silicate, with a smooth unctuous feel. In a powdered state it is sprinkled inside new gloves and in the heels of boots to produce a smooth surface and enable them to be readily slipped on.

FRENCH GREEN, EMERALD GREEN *v.* PIGMENTS.

FRENCH POLISH. A solution of shellac in alcohol; occasionally containing gum elemi and copal.

FRITTS and GLAZES. The 'glaze' of pottery is a vitreous coating, which serves to make the articles impervious to liquids, and may also be used for decorative purposes. According to the context, however, the word is also employed to denote (1) the mixed and powdered dry materials to be used for the coating, or (2) an emulsion of these materials suspended in water ('wet glaze').

Usually the glaze is applied by dipping the dry or 'biscuit' ware into this emulsion. The water soaks into the porous 'body,' leaving a deposit of the solid materials on the surface. When the ware is subsequently heated to a sufficiently high temperature, this layer melts, forming a glassy coating fused more or less completely with the underlying body of the article. Sometimes, however, the glaze is poured over the ware, or sprayed upon it, or dusted on as a dry powder, instead of being applied by 'dipping.' In the special case of salt glaze (used for stoneware), the salt is volatilised on to the ware in the kiln during firing.

The normal quantity of dry glaze on table

and toilet ware ranges from about 4 to over 9 p.c. of the weight of the ware, the average being between 6 and 7 p.c.

A good glaze should be clear, bright, and uniform; hard enough to resist wear; and in the case of domestic and sanitary articles, should withstand the action of all the ordinary acids.

Defects.—Two principal defects to which the glaze on ware is prone are (1) 'crazing,' and (2) 'scaling' or 'moulting.' In the first, a network of fine cracks spreads over the glaze; in the second, the glaze chips off at the edges. They are usually accounted for as follows:—

Broadly speaking, the coefficient of expansion of a glaze should be that of the underlying 'body.' If, on cooling, the glaze contracts much more than the body, it is under tension, and either at once or during subsequent usage it yields to the stress, and cracks. The 'crazing' may not develop for several months. In some ware—*e.g.* tiles—crazing is not of itself a serious fault; in fact, makers hold that the refraction effects which result render the ware more artistic. The purchaser, however, may be prejudiced against it; and in the case of table ware there is the additional objection that the cracks may harbour dirt and micro-organisms.

On the other hand, if the glaze contracts much less than the body, it is under pressure when cold, and portions chip off, even sometimes breaking the body itself. This 'scaling' or 'moulting' is a less frequent evil than crazing. Moreover, it usually shows itself immediately after firing, and a remedy can thus be looked for before turning out further similar goods.

Other reasons for crazing are given in some cases. Thus 'short-fired' glaze, where fusion with the body is imperfect, is prone to craze.

Either the body or the glaze, or both, may be modified to remedy crazing. In the glaze, the proportion of alkalis is diminished, or that of the lime, silica, or boric oxide increased.

Composition.—Glazes after fusion are either alkali silicates (salt glaze), or silicates and borosilicates of aluminium, alkalis, and the alkaline earths, with or without lead. In coloured glazes, various colouring oxides, *e.g.* those of cobalt, copper, iron, manganese, are also present. Before fusion, the glaze may be merely common salt or felspar; but the usual materials of glazes are certain natural silicates, namely felspar, china clay or kaolin, and Cornish stone, mixed with flint or sand, chalk, borax or boric acid, soda, white lead, red lead, and litharge. Cullet (broken glass) is also sometimes an ingredient, and for coarse earthenware glaze, galena.

Fritting. Borax, boric acid, and soda, however, being soluble in water, would pass into the porous body of the biscuit ware during dipping if they were merely mixed with the other ingredients of the wet glaze. Hence they must be made insoluble in water. This is done by fusing them with a portion of the other ingredients containing lime, alumina, and silica, and the complex borosilicate thus obtained is a 'borax fritt.'

By 'fritt,' therefore, is to be understood certain ingredients of a glaze, which have been mixed and subjected to a preliminary fusion before being ground up with the remaining materials. Occasionally, the whole of the ingredients may thus be formed into a 'fritt.'

When lead is a constituent of the glaze, fritting is also advantageous, for two reasons: (1) it can thus, with due care, be rendered almost insoluble in dilute acids, and therefore much less dangerous to the health of the workers than when in the 'raw' form of oxide or carbonate; (2) the high density of 'raw' lead tends to make it settle down in the dipping tub more rapidly than the lighter ingredients do, thus making the glaze less uniform; this tendency is largely counteracted by having the lead in the form of a fritt. This, of course, also applies to other heavy materials, such as barium carbonate. Other cases where fritting is beneficial are when an ingredient is present in very small proportion, since it is then distributed more evenly; or when certain of the constituents are fusible with difficulty at the temperature employed for 'firing' the ware. A higher temperature may be used for the fritting, and much of the chemical work done which, with the 'raw' glaze on the ware, would have to be performed at a less effective temperature.

On the other hand, a certain proportion of material in the 'raw' state, especially clay, is advantageous for keeping the glaze suspended in water for dipping; hence it is not usual for all the ingredients of a glaze to be fritted.

Formulæ of glazes. In ceramic calculations it is customary to express the chemical formula of a glaze in terms of molecular 'equivalents' the sum of the RO constituents being made unity. Thus the glaze described on p. 602 will reduce to $1RO,0{\cdot}27Al_2O_3,3.5(SiO_2,B_2O_3)$. Typical English glazes similarly work out as follows:—

	RO	Al_2O_3	$SiO_2.B_2O_3$
China . .	1	0·31	3·57
Earthenware .	1	0·26	2·80
Granite . .	1	0·32	3·43

The theoretical acids corresponding to the above four formulæ, expressed as ratios of $H_2O:SiO_2$, are respectively 1 : 2·1, 1 : 1·9, 2 : 3·1, and 4 : 7. That is, the four glazes lie between the bisilicate type ($H_2O,2SiO_2$) and the polysilicate ($2H_2O,3SiO_2$). Seger gives for white ware glazes the limits $1RO,0{\cdot}1Al_2O_3,2{\cdot}5SiO_2$ and $1RO,0{\cdot}4Al_2O_3,4{\cdot}5SiO_2$. The first is somewhat less acid than a bisilicate, the second rather more. A soft, heavily leaded English majolica glaze, however, $1RO,0{\cdot}16Al_2O_3,1{\cdot}68(SiO_2,B_2O_3)$, corresponds to $7H_2O,8SiO_2$, and is but slightly more acid than a monosilicate.

Lead glazes. The number of recipes for these is legion, but on calculating them out to the constituent oxides, they reduce to a few main types. They may be broadly classified as follows:—

(1) *China, earthenware, granite, ironstone,* and *semi-porcelain.* Contain 12–20 p.c. of PbO, occasionally more, usually about 17 p.c.

(2) *Rockingham, jet,* and *majolica.* 25–50 p.c. of PbO. Rockingham glazes contain Mn_2O_3, and jet CoO. Many majolica glazes have from 25 to 35 p.c. of PbO; the 'soft' varieties 40–50 p.c.

(3) *Tile glazes.* Usually 40–50 p.c. of PbO; the harder varieties less; in the softer kinds as much as 60 p.c.

(4) *General coloured glazes.* Described later; the proportion of PbO in these varies widely.

Examples showing the general percentage composition are:

	Granite	China	Rockingham	Jet	Soft majolica	Soft tile
SiO_2 .	54·8	50·8	35·6	34·8	32·3	32·6
PbO .	12·9	17·6	42·1	55·0	48·1	59·1
Al_2O_3 .	10·1	9·1	8·7	5·2	5·9	5·3
CaO .	4·8	5·4	2·9	1·2	3·8	0·8
Na_2O .	7·5	3·8	2·4	0·6	3·5	—
K_2O .	3·8	4·8			2·5	2·2
B_2O_3 .	6·1	8·5	0·7	—	3·9	—
Mn_3O_4	—	—	6·1	—	—	—
CoO .	—	—	—	2·1	—	—

Other things being equal, the larger the proportion of lead the 'softer' is the glaze, and the lower the temperature of firing. There is little doubt that for this reason more lead than is really necessary is often used.

Lead fritts. Lead oxides and carbonates are readily dissolved by the acid of the gastric juice, giving rise to plumbism. By suitable fritting, however, complex silicates containing lead, alkalis, alumina, and lime can be obtained of such character that, even when finely powdered, dilute acids attack them very slightly.

To be of this insoluble character, the complex silicate must not be more basic than would correspond to the metapolysilicic acid $H_4Si_3O_8$ (Chem. Soc. Trans. 79, 803–804). Preferably they should be less basic. Moreover, only a limited proportion of boric oxide appears to be admissible if the silicate contains a large percentage of lead, and the materials must, of course, be thoroughly fused. Previous fine grinding and good mixing are important in securing such fusion. Under these conditions, lead fritts may be made containing any proportion of lead up to 50 p.c. of PbO or over, but yielding only a very small quantity of lead to the action of dilute acids. The other bases may also vary considerably in their proportions, replacing one another and the lead oxide within wide limits, without notably affecting the amount of 'soluble' lead:

	PbO	Al_2O_3	CaO	$(Na,K)_2O$	PbO dissolved
1.	16·2	10·3	8·5	9·2	1·7 per cent.
2.	44·1	5·5	0·9	3·4	2·1 „

Simple lead bisilicate $PbSi_2O_5$, containing theoretically 65 p.c. of PbO, and in practice about 60–63 p.c., is also used, but is somewhat more attackable by acids than the complex silicates. Nevertheless, there are some advantages attending the use of the simple bisilicate. The proportion of PbO in it being very high, less of the fritt is required to furnish a given amount of PbO in the glaze; this leaves so much the more room for clay and other materials to be used raw, if desired, to facilitate suspension of the materials in the water of the dipping tub. It implies, too, a minimum of alteration in changing from a raw lead glaze to one with fritted lead. For example, if the 17·6 p.c. of PbO in the china glaze, mentioned in the table above, were supplied by lead bisilicate, nothing but 9·5 p.c. of SiO_2 would have to be taken from all the rest of the materials. Without pressing this point unduly—for it should not be forgotten that the complex lead polysilicates may contain as much as 50 p.c. of PbO, and still be of 'insoluble' character—its importance will easily be recognised. The bisilicate is chiefly of value for the more heavily leaded glazes, Rockingham, jet, and majolica. The quantity of 'soluble lead' (*v. post*) extractible from commercial samples of the bisilicate is from 4 to 8 p.c.; hence majolica glazes containing 30–40 p.c. of total PbO would yield only 2–5 p.c. of 'soluble lead' if compounded by means of the bisilicate.

Simple lead polysilicate, $Pb_2Si_3O_8$, yields more soluble lead than the bisilicate; and from the monosilicate, $PbSiO_3$, the whole of the lead is easily dissolved. Even the complex silicates, if of the monosilicate type, H_2SiO_3, readily yield up a large proportion of their lead to the action of dilute hydrochloric acid. Lead fritts of this (monosilicate) character were almost the only form of 'fritted lead' used in the English potteries up to a few years ago, and it is not surprising that they gave rise to cases of lead poisoning.

Complex lead polysilicates and bisilicates containing alumina yield less soluble lead than the corresponding simple lead silicates. There is evidence to show that the alumina renders the silicate more stable—perhaps by acting as an acidic oxide (Chem. Soc. Trans. 97, 2286).

Where fritts contain only small quantities of 'soluble' lead—say up to 3 p.c. or so—one treatment of the ground fritt with dilute hydrochloric acid removes nearly all this soluble lead, which there is reason to believe is usually present as an admixture of silicate more basic than the bulk. On subsequently testing the residue, mere traces of lead are extracted.

The various forms of lead fritt are heavy glass-like substances of yellow colour. They should be of uniform texture, showing no fragments of unfused materials. They have no sharp melting-points; when heated they soften gradually until fused. Vitreous silicates, however, conduct electricity (Doelter), and the relative fusibilities of fritts may be compared by determining the temperatures at which the coarsely powdered fritts soften and blend into a continuous mass, such as will allow the passage of the electrical current. As thus determined, the 'softening-points' of some simple lead silicates are as follows: PbO,SiO_2, 480°; $PbO,2SiO_2$, 570°; $PbO,3SiO_2$, 620°. The inclusion of boric acid or borax in the silicate lowers these softening-points; lime or alumina raises them (Beck, Löwe, and Stegmüller; *v.* reference at end of article).

Effect of fine grinding upon solubility of the lead. For a full discussion of this, *see* Manchester Memoirs, vol. 45 (1901), No. 15, or Parliamentary Paper Cd. 679 on Lead Compounds in Pottery, 33. The conclusion is that fineness of subdivision is not absolutely without influence upon the quantity of lead dissolved; but that within the limits of fineness occurring in actual practice the effect is too small to be of serious moment.

Method of determining the 'soluble' lead. The British official method is as follows: 1 gram of the dried glaze or fritt, ground ready for use, is shaken continuously for an hour with 1000 times its weight of 0·25 p.c. solution of hydrochloric acid. After being allowed to settle for an hour, an aliquot part is filtered off, silica separated by evaporation in the usual way, the

lead precipitated as sulphide, and finally weighed as sulphate.

In the United Kingdom potters who use no glaze yielding more than 5 p.c. of 'soluble lead' (PbO), as thus tested, are exempted from certain restrictions. Further exemptions are allowed where the glaze used gives not more than 2 p.c. of such soluble lead. If the total amount of lead is not more than 1 p.c. (calculated as PbO), the glaze is classed as 'leadless,' and this carries with it additional privileges.

Percentage composition of some complex lead silicates, with the amounts of PbO dissolved from them by 0·25 p.c. HCl :—

No.	Type	PbO	CaO	$(Na,K)_2O$	Al_2O_3	B_2O_3	SiO_2	p.c. PbO dissolved
1.	Bisilicate	21·8	8·5	3·8	7·4	3·8	54·4	traces
2.	,,	44·1	0·9	3·4	5·5	—	44·7	2·1
3.	Polysilicate	16·2	8·5	9·2	10·3	5·8	49·7	1·7
4.	,,	41·1	2·1	5·9	7·2	—	43·6	3·0
5.	Monosilicate	37·9	10·8	3·7	8·2	—	37·6	28·0
6.	,,	70·3	0·5	1·6	1·1	2·6	23·9	70·3

Fritts similar to Nos. 2 and 4 are the more generally useful for compounding glazes. Those like Nos. 1 and 3, containing less PbO and more SiO_2, have more restricted application; and Nos. 5 and 6, in so far as soluble lead is in question, are quite inadmissible.

The proportion of lead oxide dissolved from a few fritts containing 57–63 p.c. of PbO, and approximating to lead bisilicate in composition, is appended :

PbO present, p.c.	57·3	58·5	59·3	63·4
PbO dissolved ,,	2·6	4·2	5·1	7·2

If these fritts are used to supply the lead in glaze containing 15 p.c. of lead oxide, the amount of soluble lead in such glaze will range from 0·7 to 1·7 p.c.

Lead dissolved from finished ware. Lead may be extracted by acids from the glaze on the fired article, as, for example, by vinegar or fruit acids from culinary vessels. There is evidence to show that, speaking broadly, the more 'soluble' lead there is in the glaze before firing, the more it is liable to be extracted from the glaze on the finished article. The actual quantity, however, is less from the fired glaze than from the original, on account both of the smaller surface presented and of the chemical changes resulting from the fusion. A German enactment (June 25, 1887) provides that eating, drinking, and culinary vessels must not yield up lead when boiled for half an hour with acetic acid of 4 p.c. strength.

Compounding of glazes. In compounding glazes from the raw materials regard must be had to several considerations besides the formula and the analytical composition. The proportion of clay, for instance, influences the shrinking of the glaze before firing; too much causes a tendency to flake off. Again, it may be that sufficient alkali cannot be introduced as felspar or stone without adding too much alumina; some alkali must then be included as a fritt, which may also contain the borax and the lead, if these are constituents of the glaze. An example from actual practice will illustrate the compounding of a glaze by the use of fritts.

The proximate composition of a certain glaze used for earthenware and china is given[1] as: SiO_2 50·9, PbO 17·0, Al_2O_3 7·7, CaO 7·6, $(Na,K)_2O$ 6·0, and B_2O_3 10·8 p.c. To obtain all the advantages of fritting, two fritts must be made, one to contain the lead, and the other the boric oxide; for if a single fritt contained both, the high proportion of boric oxide would render the lead too easily soluble in acids, and thus one important advantage of fritting would be lost. A lead fritt is therefore made by fusing: litharge 39, flint 21, orthoclase and oligoclase felspars, each 10 parts; and a borax fritt by fusing: borax 150, flint 75, china clay 50, and whiting 50 parts. The calculated composition of these two fritts, allowing for the CO_2 and H_2O expelled on heating, is as follows :—

	SiO_2	PbO	Al_2O_3	CaO	Na_2O	K_2O	B_2O_3
Lead fritt	42·3	48·8	5·1	0·6	1·1	2·1	—
Borax fritt	43·1	—	8·5	13·1	11·1		24·2

(In practice, however, a *little* lead is lost by volatilisation and by fusion with the walls of the '*sagger*' during fritting. Actual analysis of the lead fritt showed 44·1 p.c. of PbO, the proportions of the other constituents being correspondingly increased.)

To form the glaze, these two fritts are then combined with raw materials, flint, china clay, and whiting, in the proportions: lead fritt 205, borax fritt 260, flint 81, china clay 34, and whiting 20 parts. The lead fritt, it may be noted, would have the same composition if it were made from the following ingredients: Cornish stone 25, litharge 48½, flint 25½, soda, calcined, 2 parts. This dispenses with the felspars.

Coloured glazes. So far as the glaze is concerned, coloured ware is obtained (1) by applying the colouring materials to the raw or biscuit body, which is afterwards glazed with a transparent glaze ('*under-glaze*' process); (2) by placing the colouring materials on the already glazed article, and refiring it ('*on-glaze*' process); or (3) by embodying the colour in the glaze itself ('*coloured-glaze*' method).

For the last-named process, a fritt may be made to contain the colouring oxide in chemical combination, and ground up with the other materials to form the glaze. Alternatively, a lead fritt or glaze may be taken as colourless fusible basis, and colouring oxides ground up or fritted with it.

The first of these two methods, for example, is that adopted by Messrs. Villeroy and Boch, Dresden. Their colourless[2] glaze for earthenware has the chemical formula :

$$1RO,0{\cdot}33Al_2O_3,3(SiO_2,B_2O_3)[8SiO_2 : 1B_2O_3].$$

Its molecular and percentage composition are :

	K_2O	Na_2O	CaO	PbO	Al_2O_3	B_2O_3	SiO_2
Mols.	0·25	0·75	1·50	2·00	1·50	1·50	12·00
P.c.	1·49	2·94	5·31	28·17	9·68	6·63	45·78

For convenience of dipping, 15 p.c. of the materials are left unfritted, the remainder being made into a fritt, as follows :—

	Felspar	Chalk	Litharge	Sand	Borax	Potsherds	Kaolin
Fritted	3·5	5·4	24·7	18·5	15·4	17·5	—
Raw	3·0	2·9	—	—	0·5	—	8·6

For coloured glazes, the CaO in the fritt is

[1] Almstrom, Lead Compounds in Pottery (Parliamentary Paper, C9207, p. 24).

[2] Lead Compounds in Pottery, Cd. 679, p. 21.

replaced by CoO, CuO, NiO, &c., or the Al_2O_3 by Fe_2O_3, Mn_2O_3, Cr_2O_3, U_2O_3, &c. These coloured fritts are then diluted with the colourless glaze to the desired tints.

The second method is exemplified as follows (Salvetat): The materials of a colourless flux, namely, calcium borate, flint, and red lead, are mixed in the proportions of 1 : 2 : 4; this mixture with 1–4 p.c. of CoO gives blues; with 3–14 p.c. CuO, greens; with 2–6 p.c. Fe_2O_3, yellows; and so on. All the ingredients are fritted to facilitate perfect mixture. An English colourless fritt for similar purposes is made by fritting: flint 10, china stone 9, red lead 30, and borax 4 parts; this is ground and mixed with various colouring oxides.

Enamels are opaque glazes, the opacity being due to tin oxide in suspension. In this country, however, the term 'enamels' (enamel colours) is also applied to the colours used for 'on-glaze' decoration.

White enamel may be obtained (Brongniart) by fritting calcine (=mixed oxides of lead and tin), sand, soda, and salt. Various proportions are used, a general formula being SiO_2 45, PbO 36, SnO_2 10, and NaCl 9 p.c. Coloured enamels result from the addition to this of 3–10 p.c. of colouring oxides. Thus 9 p.c. of lead antimonate, 5 of CoO, 5 of CuO, and 4 of MnO_2, give yellow, blue, green, and violet respectively.

Colours. *Under-glaze* colours are generally oxides or chromates, with flint, whiting, Cornish stone, or fluxes containing borax or lead. *On-glaze* colours are fusible glasses, composed usually of a lead borosilicate flux with colouring oxides. A common flux ('No. 8') used in this country consists of flint, borax, and red lead in the proportion of 1 : 2 : 3, but various proportions are employed.

Leadless glazes. The salt glaze used for *stoneware* has already been mentioned. For *hard porcelain*, the glazes employed are (1) 'alkaline' or felspathic glazes, consisting of silicates of alumina, alkalis, and alkaline earths, in which the alkalis preponderate over the lime and magnesia; and (2) 'calcareous' glazes, similar to (1), but in which the lime exceeds the alkalis. The materials used are pegmatite, with an addition of silica to modify the fusibility, or a mixture of felspar, quartz, and kaolin, with or without chalk.

For *soft porcelain*, *china*, and *earthenware*, glazes containing boric oxide are usually employed. One recipe for such glaze is: felspar 48·7, borax 27·0, whiting 13·5, and flint 10·8 p.c. This is fritted, and mixed with one-third of its weight of china clay to form the glaze.

ANALYTICAL COMPOSITION OF VARIOUS LEADLESS GLAZES.

	Pegmatite[1] (Sèvres)	Calcareous[1]	English[2] Minton's	English[2] Owen's
SiO_2	70·6	64·8	57·5	50·4
Al_2O_3 & Fe_2O_3	17·6	15·7	14·7	12·2
CaO	1·3	10·1	8·5	12·1
MgO	0·2	1·5	0·2	0·5
Na_2O	5·0	0·8	3·8	8·3
K_2O	4·2	5·6	4·1	2·5
B_2O_3	—	—	10·7	10·7
CO_2	—	—	—	2·5

[1] Bourry, Treatise on Ceramic Industries.
[2] Analysed in the Government Laboratory, London.

'Leadless' glazes not infrequently contain traces of lead, arising probably from their having been ground in mills previously used for lead glaze. Occasionally larger quantities are found, due to the use of flint glass as an ingredient.

Ware coated with leadless glaze may, on analysis, show traces of lead in the glaze, not only from the foregoing causes, but also from having been fired in a lead-washed sagger, or in proximity to lead-glazed goods. Lead in one form or another may be volatilised from the latter, and some of the lead vapours are absorbed by the leadless glaze. It is not difficult, however, to distinguish between such ware and that glazed with ordinary lead glaze. In the glaze removed from a definite area of the ware by means of hydrofluoric acid, the lead is determined; the proportion on leadless-glazed ware is usually less, and often much less, than 0·1 gram PbO per square decimetre; whereas that on lead-glazed table ware ranges from about 3 times to 8 times this quantity, and on heavily-leaded ware, such as tiles, it may be upwards of 40 times as much.

As regards the suitability of leadless glazes for pottery, it may be said that in all classes of ware a great many articles can be manufactured with leadless glaze, in a very high state of perfection. The cost of production in the commonest qualities is less than with lead glaze, and in some others is not appreciably greater. But in certain of the best and medium classes there is an undue proportion of 'seconds,' that is, ware not of the highest finish, and this raises the cost or lowers the quality. It is not clear, however, that this is due to anything inherent in the use of leadless glaze. For certain colours and methods of decoration leadless glazes at present cannot replace those made with lead. On the other hand, there is no doubt that a great deal of white and cream-coloured ware for domestic, sanitary, and electrical purposes, now coated with lead glaze, could be glazed without the use of lead.

For a summary of present knowledge and experiments respecting soluble lead in fritts and glazes, *see* Beck, Löwe, and Stegmüller, Zür Kenntniss der Bleihaltigen Glasuren und deren Bleiabgabe an saure Flüssigkeiten (Arbeiten aus dem Kaiserlichen Gesundheitsamte, Band 33, Heft 2, 1910.) C. S.

FRUCTOSE *v.* CARBOHYDRATES.

FUCHSIA. The chlorides of α- and β-dialkylsafranines are met with in commerce under this name (*v.* AZINES).

FUCHSIN, RUBIN, ROSEIN, MAGENTA (*v.* TRIPHENYL METHANE COLOURING MATTERS).

FUCOSE. CARBOHYDRATES.

FUCOSOL. This product which Stenhouse obtained by the distillation of certain *algæ* with dilute sulphuric acid (Proc. Roy. Soc. 20, 80), and which he considered as isomeric with furfurol, has been shown by Bieler and Tollens (Ber. 1889, 3062) and by Maquenne (Compt. rend. 109, 571) to be a mixture of furfurol and methyl-furfurol derived from pentaglycoses contained in the *algæ* (*v.* also Muther and Tollens (Ber. 1904, 298).

FUEL. This term includes all combustible substances obtainable in bulk which may be burned by means of atmospheric air in such a

manner as to render the heat evolved capable of being economically applied to domestic or industrial purposes. Fuels may be divided into (a) *solid fuels*, including (i.) natural fuels, consisting of woody tissues in an unaltered (wood) or an altered form (peat, lignite, coal); (ii.) carbonised fuels (charcoal, coke); (iii.) compressed fuels (briquettes); (b) *liquid fuels* (petroleum, benzenes, alcohol); (c) *gaseous fuels* including (i.) natural gas; (ii.) gases produced by the carbonising of solid fuels (coal gas, &c.); (iii.) gases produced by the partial combustion of solid fuels (blast furnace gas, producer gas, water gas). All fuels, having been originally derived from some form of living matter, or the products of its alteration, are composed of the elements C, H, O, N, &c., together with (in the case of solid fuel) a variable amount of mineral matter, which constitutes the incombustible ash.

The economic importance of a fuel depends upon (1) its distribution; (2) its cost of production, transport, and storage in bulk; (3) the total amount of heat obtainable on burning unit weight of it; and (4) the rapidity, efficiency, and smokelessness of its combustion with atmospheric air. Of all natural fuels coal is by far the most important, for despite the probability that there is much more combustible matter in the peat deposits than in all the known coalfields of the world, and the marked inferiority of coal to petroleum in respect of calorific value, no other fuel combines so many economic advantages as coal.

The calorific value, or the total amount of heat obtainable by the combustion of a given fuel, is expressed by the number of parts by weight of water which may be heated through 1° on the thermometric scale by the combustion of one part by weight (or, in the case of gaseous fuels, by volume at N.T.P.) of the fuel under conditions such that the whole of the heat of combustion is transferred without loss to the water, and that the products leave the system at atmospheric temperature and pressure. The metric unit of heat adopted for technical purposes (the K.C.U.) is the quantity of heat required to raise 1 kilog. of water through 1°C. in the neighbourhood of 15°C., whilst the British unit (the B.Th.U.) is the amount of heat required to raise 1 lb. of water through 1°F. in the neighbourhood of 60°F. Thus, 1 K.C.U. =3·9683 B.Th.Us., and 1 B.Th.U.=0·252 K.C.U.; moreover, in the case of solid or liquid fuels, a calorific value of xK.C.Us. per kilog. is equivalent to 1·8 x B.Th.Us. per lb. (or, conversely, xB.Th.Us. per lb.=0·5555 xK.C.Us. per kilog.,) whilst, in the case of a gas, xK.C.Us. per cubic metre is equivalent to 0·11236 xB.Th.Us. per cubic foot (or, conversely, xB.Th.Us. per cubic foot =8·90 xK.C.Us. per cubic metre). For purposes of calculation, the calorific value of a gas may often be expressed more conveniently in K.C.Us. per gram-molecule (*i.e.* 22·38 litres at 0°C. and 760 mm.) than in any other form; in such a case, xK.C.Us. per gram-molecule =44·68 xK.C.Us. per cubic metre at 0° and 760 mm., or 5·02 xB.Th.Us. per cubic foot at 0° and 760 mm.

In cases where hydrogen enters into the composition of a fuel, it is usual to differentiate between its *gross* and *net* calorific values, the former implying that the products of combustion have all been cooled down to atmospheric temperature (15°C.), the latter, that the heat liberated by the condensation of the steam produced on combustion and by the subsequent cooling of the water to 15° has not been included. The difference between *gross* and *net* values will always be 11·196 K.C.Us. per gram-molecule of steam produced on combustion (=622 K.C.Us. per kilog., or 1119·6 B.Th.Us. per lb.).

The determination of the calorific value of a solid or liquid fuel may be best carried out by burning a known weight of it in compressed oxygen in some form of bomb calorimeter, that known as the Berthelot-Mahler apparatus being well adapted for this purpose. In the hands of an experienced worker, the method is a very accurate one, provided that all the proper 'corrections' (*e.g.* for 'cooling' and for the formation of nitric acid) are determined and applied; it must be remembered, however, that the method gives the heat of combustion under '*constant volume*' and not under '*constant pressure*' conditions, and in the calculation of the latter from the experimental results a proper 'correction' must be applied. In the case of coals, of which combustion is attended by very little change in chemical volume (*e.g.* 1 lb. of a coal containing C=80·0, H=5·5, S=1·0, N=1·5, O=5·0, and ash =7·0 p.c. requires 136 cubic feet of air, and yields 130·8 cubic feet of gaseous product at 0° and 760 mm.), the difference between the heats of combustion under 'constant volume' and 'constant pressure' is negligible in practice, but not so in the case of a hydrocarbon such as heptane

$$C_7H_{16}+11O_2=7CO_2+8H_2O.$$

The calorific value of a gas is usually determined by burning a measured volume of it at atmospheric pressure in a chamber surrounded by a system of coils or the like, through which a flow of water at a constant 'head' is maintained. By suitable regulation of the pressure and flow of the gas and water supplies respectively, the gas may be completely burnt and the heat developed transferred substantially without loss to the water, the products leaving the apparatus at a temperature only slightly above that of the atmosphere. Several forms of this apparatus are in use, the most satisfactory being those designed by Junkers and C. V. Boys respectively. With suitable modification (*e.g.* the provision of a differential thermojunction arrangement for registering the rise in temperature of the water on a moving chart), the method can be made a 'recording' one.

The heat of combustion of amorphous carbon is 8080 K.C.Us. per kilog. when completely burnt to the dioxide, and 2417 when burnt to the monoxide; the values for the principal single gases (taken from Julius Thomsen's researches) are as follows:—

	K.C.Us. per gram molecule		B.Th.Us. per cub.ft. at 0° and 760 mm.	
	Gross	Net	Gross	Net
Hydrogen .	68·4	57·2	343·3	287·2
Methane . .	212·0	189·5	1064·0	951·3
Ethane . .	370·5	336·9	1860·0	1691·0
Ethylene .	333·3	310·9	1673·0	1561·0
Propylene .	492·7	459·1	2474·0	2305·0
Acetylene .	310·0	298·8	1556·0	1500·0
Carbon monoxide	68·0		341·4	
Cyanogen .	259·6		1303	

The *gross* values for single liquid fuels, in K.C.Us. per kilog. are *n*-hexane=11,620, benzene =10,250, toluene=10,390, methyl alcohol=5694, ethyl alcohol=7400. According to Julius Thomsen, an increase of $>CH_2$ in ascending an homologous series of hydrocarbons or alcohols corresponds to a constant increase of 158·5 K.C.Us. in the gross value of the molecular heat of combustion.

It is not possible to calculate the calorific values of compound fuels such as coal or petroleum from their elementary analyses, since the heat of combustion of a compound is never equal to the sum of those of its elements taken proportionately. In the case of bituminous coals empirical formulæ, such as:

$$Q=\tfrac{1}{100}[8080C+34{,}400(H-\tfrac{1}{8}O)+2250S]$$

K.C.Us. per kilog., where C, H, O, and S=percentage of carbon, hydrogen, oxygen, and sulphur, have been proposed for this purpose; but they cannot be considered as more than approximately correct. On the other hand, since the properties of a gaseous mixture are additive in respect of its constituents, the heats of combustion of gaseous fuels of which the composition has been accurately determined by analysis (and this applies more particularly to such cases as water gas or producer gas, the combustible constituents of which are hydrogen, carbon monoxide, and methane only) may be calculated from those of their constituents. In the case of coal gas, where the composition of the heavy hydrocarbons absorbable by bromine is always uncertain, this rule is not strictly applicable, although numbers calculated on the assumption that the heavy hydrocarbons have an average calorific value equal to that of propylene C_3H_6, are generally not widely different from those determined by the calorimeter.

The so-called 'calorific intensity' of a fuel is an unscientific term, inasmuch as the highest temperature which a particular fuel is capable of producing depends entirely upon circumstances which are, to some extent, indefinable, and difficult of control. The notion that the calorific intensity of a fuel may be deduced by dividing its calorific power by the mean specific heat of its products, is misleading, inasmuch as (1) the specific heats of gases, and especially of steam and carbon dioxide, increase with temperature, and at high temperatures are as yet not accurately known; (2) part of the potential energy of a fuel is directly radiated away during combustion, and does not appear as sensible heat in the products; and (3) combustion is ordinarily not sufficiently instantaneous to warrant the assumption above referred to. The measurement of furnace temperatures and the like is, however, of great practical importance, and many instruments have been designed for this purpose (*see* PYROMETRY). These depend upon (1) the variations with temperature in the pressure (at constant volume) or volume (at constant pressure) of a gas which does not appreciably deviate from Boyle's law (air thermometer); (2) the production of thermo-electric currents (thermojunction methods); (3) the increase in the electrical resistance of a platinum wire with temperature (resistance methods); and (4) the variation with temperature of the radiation emitted by an incandescent solid as defined by Stefan's law (*radiation pyrometry*). Methods (1) to (3) inclusive, whilst capable of great accuracy, are practically useful up to temperatures of 1000°–1200° only; they can be made 'recording,' however, and are invaluable for recording the temperatures of hot gases passing into furnaces from 'regenerative' systems (hot-blast stoves, melting-furnace regenerators) or of hot products passing into chimneys. Method (4), whilst of relative significance only, is invaluable for temperatures higher than 1000°; as a modification of method (4) may be mentioned various forms of *optical pyrometers*, in which the light emitted by an incandescent surface is compared with that from a standard source (*e.g.* an amyl acetate flame).

A. SOLID FUELS.

1. *Natural Fuels.*

All natural fuels of this class have originated in cellulose $n(C_6H_{10}O_5)$, which, in fact, constitutes about 95 p.c. of dry woody tissue. The gradual transformation of this substance into coal has proceeded during nearly all geological epochs; in the N. hemisphere the most important coal-measures occur in the Primary (Carboniferous) series; Mesozoic coals are more abundant in the S. hemisphere, whilst Tertiary coals (lignites) are found in practically all latitudes. The plants concerned in the formation of coal have varied in different geological epochs; thus ferns or their allies were largely concerned in the formation of the Primary coal-measures, and it is demonstrable that in certain cases entire beds of coal have been formed from spores. The Mesozoic coals of N. Europe are probably composed in large part of the remains of gymnospermous plants (cycads, conifers), and coniferous wood has been found associated with Antarctic coal-seams.

At one time it was generally believed that coal formation had taken place upon the actual site of growth, the requisite conditions being dense forests in swampy areas, together with oscillations of level, the coal-measures produced during a period of subsidence being overlaid by beds of water-deposited clay or sandstone, which, on re-elevation, formed the soil for renewed forest growth. Hence coal is found in strata of undoubted estuarine or lacustrine origin (Carboniferous, Jurassic, Cretaceous); the common occurrence of 'under-clays' in the coal-measures is cited in support of this hypothesis, which probably is true for some British coal-fields. It has been contended by some geologists that in many cases the transformation of vegetable *débris* into coal has taken place not upon the site of growth, but after transportation by river currents and deposition in deltas; it has also been suggested that certain coal-seams are of marine origin.

There has also been much speculation and diversity of opinion as to the nature of the transformation process, and the factors operative therein; it is usually supposed that its earlier stages were characterised by slow oxidation under water or other covering sufficient to protect the decayed wood from direct atmospheric action, and that supervening upon this were changes gradually brought about by increasing pressure and temperature as the

deposits were overlaid and 'blanketed' by accumulating newer *strata*. The final transition from a bituminous coal to anthracite—if such, indeed, has taken place—may be attributed (i.) to intense earth pressure accompanied by seismic disturbance; or (ii.) to the later intrusion of igneous matter from below. It should, however, be stated that in some instances at least there are grounds for believing that anthracite has been formed from vegetable matter of a kind distinct from that concerned in the formation of bituminous coal, without necessarily passing through the intermediate 'bituminous' stage (*vide* section of this article on British Coal Fields (1) *South Wales*, p. 612). M. Renault, from an extensive study of peat formation, has advanced the hypothesis that the chief agents in the early stages of the transformation process have been certain aërobic fungi, and anaërobic bacterial ferments, the relative activities of which would depend upon the varying water level in the bog and the formation of ulmic acid. He represents the transition from cellulose into bituminous coal by the equation:

$$4C_6H_{10}O_5 = C_9H_6O + 7CH_4 + 8CO_2 + 3H_2O.$$

(C_9H_6O would contain C=83·1, H=4·6, O =12·3 p.c., which approximates to the composition of many bituminous coals.) But whatever may have been the nature of the process, it is generally agreed that the existing coal-measures represent some 20–25 p.c. only of the weight of the original cellulose, and less than half of its heating value; in a few cases, where the original vegetable *débris* has undergone local 'petrifaction,' it has been established that the shrinkage in bulk during transformation into coal has been of the order 9 : 1 approximately. The composition and calorific values of the dry ashless cellulose and intermediate products up to coal itself is shown in the following table:—

	C	H	O and N	K.C.Us. per kilog.
Cellulose .	44·5	6·2	49·3	4167
Wood .	50·0	6·0	44·0	4000–4300
Peat .	50–64	4·5–6·8	28·6–44·0	5000–6000
Lignites .	60–75	5·0	20·0–35·0	6000–7000
Bituminous coals .	75–90	4·5–5·5	5·5–15·0	8000–9600
Anthracite	90–95	2·4	3·0	9200–9800

Wood when dry consists of about 95 p.c. of cellulose and 4 p.c. sap, associated with a small amount of mineral ash (chiefly $CaCO_3$ and K_2CO_3). Recently felled timber contains a large proportion of water which 'air-drying' reduces to about 20 p.c. An 'air-dried' wood is classed as 'hard' or 'soft' according as its sp.gr. exceeds or falls below 0·55; 'hard' woods are less inflammable than 'soft' varieties. As a fuel wood is very combustible, and burns with a great amount of flame; it is well adapted for domestic fires and the firing of tubular boilers, its low content of infusible ash making it a clean fuel without a vestige of 'clinkering' properties. Owing to its large content of hygroscopic water, it is quite unsuitable for the attainment of high temperatures, unless it first be carbonised (charcoal), or be gasified in a producer. On distillation in closed retorts or chambers it yields, under favourable conditions, 20–25 p.c. of charcoal, 9–13 p.c. of tar, 40–45 p.c. of crude 'pyroligneous acid' (corresponding to 2–4 p.c. anhyd. acetic acid), and 22–32 p.c. of inflammable gases. The chief timber-producing countries are the Russian Empire with 920 million acres of forests (575 in Europe and 350 in Asia), Canada with 800 million acres (of which probably less than half represents timber of commercial value), the United States, Norway, and Sweden with 70 million acres, and Germany with 35 million acres. Russia is, however, the only European country which produces more timber than it requires. The rapid demolition of the world's timber reserves is becoming a serious economic problem, and it is improbable that wood will ever again take important rank as a fuel.

In countries where wood, peat, or coal is scarce, vegetable refuse (cotton stalks, brushwood, straw, &c.) is used as fuel for tubular boilers; as a rule it has between 70 and 80 p.c. of the heating value of dry wood.

Peat is a widely distributed and abundant fuel of great future potentiality, it being estimated that the amount of combustible matter in the world's peat deposits exceeds that in all the known coal-fields. It is principally found in high latitudes; one-seventh of the area of Ireland is covered with peat, whilst in Great Britain there are about 6 million acres covered to an average depth of about 12 feet. Extensive deposits occur in Russia, where peat is an important metallurgical fuel, in Scandinavia, N. Germany, Bavaria, Austria, Italy, and N. France, to mention European countries only. These deposits vary considerably in age, the oldest peat having a dark-brown or black colour, with but merest traces of its original organic structure, whilst the recent varieties are light-brown in colour, of spongy texture, with distinct vegetable structure; unlike wood, it contains a fairly large and variable proportion of mineral ash (5–15 p.c. as a rule) of (usually) infusible character. The composition of the ash varies considerably; sulphate and carbonates of lime and magnesia, ferric oxide, and silica being usually the most prominent constituents. The difficulty in the way of utilising the potential energy of peat for economic ends lies in the fact that even a well-drained peat-bog contains 80–90 p.c. of water, which can only be to a small extent pressed out mechanically, and for the evaporation of which more energy would be required than is represented by the whole fuel value of the bog. Consequently, 'air-drying' has hitherto been universally resorted to, but as this can only be carried out during the summer months, and must obviously depend upon climatic conditions, it cannot be considered seriously as a means of preparing large quantities of peat for the market. Moreover, 'air-dried' peat still contains from 15–25 p.c. of water, its calorific value (which varies between 2235 and 4307, with an average of about 3000 K.C.Us. per kilog.) is usually considerably less than half that of a bituminous coal, whilst bulk for bulk its heating power probably does not exceed one-eighth that of coal. Dry 'ashless' peat contains C=50–64, H=4·7–6·8, O=28–44, and N=0·5–2·5 p.c., its cal. value =5200 K.C.Us. per kilog., and its sulphur content is low.

As recently as 1905 the Royal Commission

on Coal Supplies reported that '*in order to make the manufacture of peat fuel a success in this country, it is necessary that some process should be discovered by which the moisture can be got rid of without "air-drying," and at a cost which would not be prohibitive; at present there is no such process.*' In 1909, however, the late Dr. M. Ekenberg announced his process of '*wet carbonisation*' as a practical solution of the problem (Jour. Iron and Steel Institute, 1909, i. 313). This process is based upon his discovery that 'peat substance' consists of vegetable *débris*, the cells of which contain and are surrounded by a slimy '*hydrocellulose*,' formed by prolonged contact of the original cellulose with water. Although this constituent is present to the extent of 0·2–1·2 p.c. only, it is in the form of an enormously swollen jelly of the consistency of soft-soap, and containing as much as 25 times its own weight of water. When submitted to pressure, it may be forced through the interstices of stout canvas quite unchanged. It is, however, rapidly hydrolysed by water at 150°–200°, forming the soluble dextrose, and peat pulp so hydrolysed readily parts with its water under hydraulic pressure. The Ekenberg process (as originally proposed) consists in forcing a peat pulp containing 12½ p.c. of peat substance and 87½ p.c. of water at 220–300 lbs. per sq. in. pressure through a series of tubes heated externally to about 200°, the operation being combined with a system of heat recuperation, whereby the outgoing hot 'carbonised' peat imparts heat to the incoming cold pulp. The 'carbonised' pulp is dehydrated by mechanical pressure, and the dehydrated fuel is subsequently briquetted. The resulting briquettes of 'peat coal' have a black glossy surface, and a sp.gr. of 1·29–1·35; owing to their regular shape, their volume weight is considerably greater than in the case of coal; one ton of briquettes occupies about 30 cub. ft. They burn with a long smoky flame and are easily lighted; with a good chimney draught it is claimed that their combustion is smokeless. A sample, analysed by the writer, contained C=58·35, H=5·42, N=1·7, ash =7·8 p.c., and had a cal. value 5987 K.C.Us. per kilog. On being carbonised in a retort, 'peat coal' yields 14,850 cub. ft. of 20·6 candle-power gas (free from CO_2); it also makes an excellent gas-producer fuel.

Peat containing as much as up to 60 p.c. moisture has been successfully gasified on a large scale in gas producers under ammonia recovery conditions (*vide* PRODUCER GAS); the following results have been obtained on Mond plants:—

Origin of peat	German	Italian	English
Per cent. moisture .	40–60	45	57·5
,, nitrogen .	1·0	1·58	2·3
Yield of gas in cub. ft. at 0° and 760 mm. per ton peat . .	85,000	60,000	90,000
Gross cal. value of gas B.Th.Us. per cub. ft. at 0° and 760 mm. .	150	166	134

The richness of the gas depends upon the moisture in the peat; where the moisture is not excessive, the gas may contain as much as 35–40 p.c. of combustible constituents, *e.g.* 9·8CO, 23·2H_2, 4·8CH_4, with 20·3CO_2. About half of the total gas is required to fire the boilers and superheaters on the plant, the remainder being available for heating or power purposes outside the plant. In addition to ammonium sulphate, it is possible to recover other by-products (tar, acetate of soda or lime, acetone, wood spirit).

Lignite (brown coals). Under this general term are included principally Tertiary coals (intermediate between peat and the true coal), which are widely distributed over the Central European plain and the southern states of N. America (Texas, Arkansas, and Louisiana); Cretaceous coals of the lignite class occur over a large area between lats. 49° and 43° N. and long. 100°–107° W. (the states of N. Dakota, Montana, and Wyoming) of N. America. Classified according to external characters and geological age, lignites are usually divided into (1) woody or fibrous brown coal, with a distinct ligneous structure; (2) earthy lignite devoid of organic structure and easily powdered; (3) common brown coal, with a slatey cleavage and dark-brown colour, *e.g.* Bovey coal; and (4) bituminous lignite, pitch black in colour, and having a conchoidal fracture. Lignites are of little economic importance except in Germany and Austria-Hungary, where (in 1909) 68·5 and 26 million tons respectively were raised for home consumption. Freshly-mined lignites may contain up to 50 p.c. of water, which, on air-drying, is reduced to usually between 10 and 20 p.c.; many varieties, when completely dried, crumble to powder, which, however, may be again consolidated into a serviceable block fuel by pressure. The ash content usually varies between 5 and 15 p.c., but may run considerably higher. The composition of the dry 'ashless' fuel varies between the following limits: C= 60–75, H=5, O=19–34, N=0·5–1·5 p.c., and it has a calorific value of 6000–7000 K.C.Us. per kilog. Lignite burns with a very long smoky flame, and is generally non-caking (*i.e.* it does not yield a coherent coke); it is largely used in Germany and Austria for firing boilers, and for the heating of evaporating pans, the better qualities being sometimes used for metallurgical purposes. Like peat, it may be gasified in producers.

Bituminous coal. This term is applied to a whole series of 'flaming' coals of Primary or Mesozoic origin, and it includes all the economically important coals except anthracites. More than 90 p.c. of the world's total output of 1025 million tons of coal in 1909 (including anthracites, but excluding lignites) was due to six countries (United States 437·2, Great Britain 263·75, Germany 148·9, France 37·25, Russia 24·1, and Belgium 23·5 million tons respectively). Taking a series of eight quinquennial averages over the period 1870–1909 inclusive, the output of coal in Great Britain has increased from 121·2 to 256·0 million tons per annum, whilst the annual consumption per head of population has increased from 3·396 to 3·965 tons. It is estimated that the available supplies within 4000 feet of the surface in Great Britain amount to about 550 times her present annual output, whilst the world's known reserves (90 p.c. of which are in the United States and China in the ratio of 4 : 3) probably

amount to about 4000 times the present annual consumption.

For commercial purposes, bituminous coals are classified according to their suitability, or otherwise, for certain specific economic ends, *e.g.* steam raising, furnace firing, gas making, manufacture of dense metallurgical coke, and the like. The usefulness of any given coal for a particular purpose depends principally upon (1) its content of 'volatiles' expelled at 900°–1000°, which largely determines the length and character of the flame emitted during vigorous combustion; and (2) the character of the carbonaceous residue after the 'volatiles' have been expelled at high temperature, which doubtless in part depends upon the nature and mode of decomposition of a certain 'cementing' constituent of the coal, and partly also upon the character (fusibility) of the mineral ash associated with it. For economic purposes, Percy proposed to class bituminous coals as (1) non-caking, free burning, rich in O; (2) caking; and (3) non-caking, rich in C. Several classifications have been proposed based upon the ultimate composition of the dry and ashless coals; of these probably the most useful is that generally attributed to the French metallurgist Gruner, but in reality due originally to Regnault, as follows:—

Class	Chief uses	Composition[1] C	H	O and N	Cal.[1] value	P.c. and character of carbon residue (coke)
I. Non-coking long-flame	Reverberatory furnaces	75–80	4·5–5·5	15–20	8000 / 8500	55–60: pulverulent
II. Coking long-flame	Gas manufacture and reverberatory furnaces	80–85	5·6	10–15	8500 / 8800	60–68: coherent but very porous
III. Coking or furnace coals	Coking	84–89	5·0–5·5	5·5–11·0	8800 / 9300	68–74: fairly dense coke
IV. Short-flame coking coals	Coking: steam raising	88–91	4·5–5·5	5·5–6·5	9300 / 9600	74–78: very dense coke
V. Short-flame non-coking (anthracitic)	Domestic purposes, steam raising	90–93	4·0–4·5	3·0–5·5	9000 / 9500	82–92: pulverulent

Some authorities regard the Regnault-Gruner classification as defective, in that it is based chiefly on the 'oxygen' content of the coal, which bears all the analytical errors, and also in that it underrates the importance of hydrogen. Fleck, who introduced the idea of 'disposable hydrogen' (*i.e.* hydrogen left after deducting that equivalent to oxygen), proposed, as a basis of classification, the factor $\frac{100\left(H-\frac{O}{8}\right)}{C}$; and Campbell, of the U.S. Geological Survey has proposed 100H/C. Wedding divides coals into six groups, according to the percentage of volatile matter yielded in the dry ashless condition, as follows: (1) lean anthracitic coals, 5–10; (2) sinter coals, poor in gas, 10–15·5; (3) caking coals (old), poor in gas, 15·5–33·3; (4) caking coals (recent), rich in gas, 33·3–40·0; (5) sinter coals (recent), rich in gas, 40·0–44·4; (6) sand coals (recent), rich in gas, 44·4–50. It is, however, clear that pending a much fuller knowledge than we now possess respecting the proximate constituents of coal, none of the above classifications can be considered satisfactory in any final sense.

In the selection of a coal for any particular purpose, the following points should be borne in mind: (1) the best '*gas coals*' are those in which the ratio O : H is approximately 2·0; they yield from 30 to 38 p.c. 'volatiles' (reckoned on the dry ashless coal), and a fairly porous coke of no great strength; (2) the best '*coking coals*' usually yield between 20 and 30 p.c. of 'volatiles,' and are strongly caking; the best '*steam coals*' yield less than 20 p.c. of volatiles, are, as a rule, non-caking and smokeless, or nearly so in their combustion; (4) for '*gas-producer*' purposes it is desirable that a coal should be non-caking, and have an infusible ash. The caking properties of a coal depend upon its containing certain organic compounds (extractable by means of pyridine) which decompose when heated, yielding 'volatiles' and a small amount of a pitch-like cement which acts as a binding material in the resultant coke; *ceteris paribus*, a caking coal with a fusible ferruginous ash will yield a stronger coke than one of similar age and composition with a highly silicious ash. Non-caking or feebly caking coals are either (1) those of greatest age, high in carbon and low both in oxygen and 'volatiles'; (2) those of comparatively recent origin, with a high oxygen content; or (3) those from '*oxidised*' seams which have at some period been exposed to atmospheric influence. Variations in the thickness of the overlying strata seem to influence the coking properties of a weakly caking coal-seam; according to Wedding, whilst coals of classes 1 and 2 (in his classification) show more prominent coking properties the thicker the superincumbent strata, the opposite holds good for coals of classes 5 and 6. For coking purposes, it is often advantageous to mix a weakly caking, short-flame coal, rich in carbon, with one which cakes well but yields much gas. Finally, it should be observed, that a caking coal loses its coking properties on prolonged exposure to the atmosphere.

Besides the elements already referred to, coal (ashless) contains two others of importance, viz. nitrogen and sulphur. The nitrogen, although present to an extent of between 1 and 2 p.c. only, is of great economic value, since it is the source of 95 p.c. of the world's entire output of ammonium salts. As the results of exhaustive

[1] The numbers given refer to the *dry* "ashless" fuel.

tests upon some 80 Scottish coals (N=0·915–1·873 p.c.) at the Provan Gasworks, Glasgow, it has been found that under the conditions prevailing during distillation in a modern gas retort, about 58·3 p.c. of the total nitrogen remains in the coke, 19·5 p.c. appears as N in the gas, 17·1 p.c. is obtained as ammonia, 3·9 p.c. passes as organic bases into the tar, and, finally, 1·2 p.c. is evolved as cyano- compounds. Also, as the results of coking a Durham coal containing 1·57 p.c. N in Otto Hilgenstock ovens at Blayden-on-Tyne, A. Short (J. Soc. Chem. Ind. 1907, 581) found that 43·31 p.c. of the N remained in the coke, 15·16 p.c. was recovered as NH_3, 2·98 p.c. appeared in the tar, 1·43 p.c. as cyano- compounds, the remaining 37·12 p.c. representing N in the gas. The temperature at which the evolution of ammonia begins when coal is heated seems to depend on its geological age. Carrick-Anderson, and Roberts (J. Soc. Chem. Ind. 1899, 1099) give 333° as the lowest temperature for NH_3 evolution from a young gas coal, and state that with coal of an older type it may rise to about 480°. Hilgenstock has found that the principal evolution of NH_3 occurs after the caking stage of the distillation has set in. M. G. Christie (Inaug. Diss. Aachen, 1908), in an investigation upon peat, gas coals, and anthracites, has shown that evolution of NH_3 begins at about 350° in the case of a gas coal, and at 450° in the case of anthracites, and that the principal evolution occurs between 500° and 700°; according to Christie, also, that part of the N which remains in the coke is present in an extraordinary stable '*nitride*' form, and is only slowly expelled as the temperature is raised from 900° to 1900°. From this it would appear that the N is present in at least two distinct forms, viz. (i.) as organic compounds which decompose at a temperature below 900°, and (ii.) in a stable 'nitride' form.

Sulphur must always be considered as a deleterious element in coal; it appears in three forms, namely, (i.) as pyrites FeS_2; (ii.) as sulphates (gypsum); and (iii.) as '*organic*' sulphur. Although partly expelled (chiefly as H_2S, CS_2, and thiophen) on distillation, the sulphur is largely retained (chiefly as FeS and CaS) in the coke; it is impossible to produce a coke low in sulphur from a coal whose ash is rich in Fe, Ca, or Mg compounds. According to A. Short (*l.c.*), in caking a Durham coal containing 0·824 p.c. S, in by-product ovens, 72·5 p.c. of the S remained in the coke, 24·0 p.c. was evolved as H_2S, 1·45 p.c. passed into the tar, the remaining 2 p.c. being accounted for as gaseous products other than H_2S.

Coal, when freshly mined, may contain much water ('pit water') and some occluded gas. Most of the water is rapidly lost on air drying, whilst the remainder (usually some 2–3 p.c.) is completely lost at 105°. The occluded gas may be withdrawn by continued exhaustion at the ordinary temperature; from a Durham coal (Hutton seam) Bedson obtained 1·6 c.c. of gas per gram of coal; the gas contained CO_2=4·35, CH_4=71·15, C_2H_4=6·65, O=2·80, and N =15·05 p.c. From a Lancashire coal (Lower Mountain Mine), R. V. Wheeler obtained 1·375 c.c. of gas per gram, containing NH_3=0·5, H_2S=0·5, C_2H_4=0·4, CO=2·1, C_2H_6=8·10, CH_4=80·35, O=0·4, and N=7·65 p.c.

The mineral ash in coal varies greatly in amount, colour, composition, and fusibility. A distinction must be drawn between the heavier mineral matter, 'dirt' (pyrites sp.gr. 5·0, shale sp.gr. 2·5, and gypsum sp.gr. 2·3), often mixed with freshly mined small coal (sp.gr. 1·2–1·3) from which a separation can be effected by mechanical washing, and the true or 'fixed' ash of the coal, which is disseminated throughout its entire mass, and cannot be so removed. A pure white ash which the writer once obtained from an Australian coal contained 53·4SiO_2, 44·0Al_2O_3, together with some 2 p.c. only of lime and the merest traces of ferric oxide. Usually the ashes of coals contain, in addition to Al_2O_3 and SiO_2, variable proportions of CaO, MgO, Fe_2O_3, and SO_3 (chiefly as $CaSO_4$); the colour varies from cream or light-buff to red-brown, according to the iron content, and, as a rule, the fusibility increases with the darkening colour. The ashes of a typical Lancashire coal will contain SiO_2=25–40, Al_2O_3=19–28, Fe_2O_3=22–32, CaO=3–16, MgO up to 3·5, and SO_3=3–8 p.c. A fusible ferruginous ash is a constant and prolific source of clinkering troubles in furnaces and gas producers.

Whilst the majority of organic solvents (ether, alcohol, chloroform, benzene) have but little effect upon coal, Bedson has called attention to the remarkable solvent action of pyridine (J. Soc. Chem. Ind. 1908, 27, 147). The coal should be ground so as to pass through a sieve of 1000 apertures per sq. inch, then mixed with sand and extracted with the solvent in a Soxhlet apparatus. The residual carbonaceous material is always quite devoid of coking properties. Careful trial has shown that the amount of material extracted corresponds nearly to the yield of 'volatiles' when the coal is carbonised out of contact with air at 750°.

The work of R. V. Wheeler and Burgess upon the volatile constituents of coal (Chem. Soc. Trans. 1910, 97, 1918; 1911, 99, 649) has thrown an interesting light upon the chemical nature of coal; the behaviour of anthracitic, semi-bituminous, and bituminous coals at definite temperatures between 450° and 1100° was carefully investigated; it has been established (1) that at low temperatures (up to 450°–500°) higher paraffins, C_3H_8, C_3H_8, C_4H_{10}, &c., as well as methane, are conspicuous decomposition products, whereas H is produced in very small quantity; (2) that the evolution of paraffins ceases entirely at about 700°, the absolute amount of CH_4 reaching a maximum at 800°–900°; and (3) that between 700° and 800° there is a 'critical point' above which the evolution of H abruptly and rapidly increases. It seems probable that coal contains two types of compounds, having very different degrees of stability; the least stable type decomposes at temperatures between 400° and 700°, yielding chiefly paraffin hydrocarbons, but no hydrogen, whilst the more stable type requires a higher temperature than 700° for rapid decomposition, and yields chiefly hydrogen. It would also seem probable that the more stable 'hydrogen yielding' type of constituent is essentially a degradation product of cellulose, whilst the less stable 'paraffin-yielding' constituents are derived from the gums and resins originally contained

in the sap of the coal plants, and form 'cement' of a conglomerate of which the cellulose derivatives are the base. The differences between one coal and another may thus depend on the relative as well as the absolute proportions in which these two types of compound exist in the coal.

When bituminous coal is charged into a hot furnace, it first of all undergoes a process of destructive distillation; its least stable resinous constituents decompose, and hydrocarbons are freely evolved, which, on partial oxidation or secondary decomposition, give rise to carbon, together with minute quantities of dense tarry vapours (smoke) which are difficult to burn, except in an abundant air supply and at high temperatures. The residual 'semi-carbonised' fuel, being raised to incandescence, is burnt by the air, which is drawn in through the grate. If, as in intermittent stoking, the furnace be cooled by a sudden inrush of cold air during the introduction of a fresh charge of fuel, smoke will be freely evolved. The production of smoke may be greatly reduced by the adoption of continuous mechanical stoking, especially if it be on the 'under-feed' principle, or by making the mixture of 'smoke' and *hot* air impinge upon an incandescent fireclay surface; the introduction of a pre-heated secondary air supply near or at the fire bridge of the furnace will often diminish smoke. It is never possible to burn coal in a furnace with the theoretical quantity of air; thus 1 lb. of coal containing C=80·0, H=5·5, S=0·9, N=1·5, O=5·0, and ash =7·0 p.c., would, theoretically, require 136·0 cub. ft. of dry air at 15° and 760 mm. for complete combustion, and the cooled gaseous products would contain 18·2 p.c. CO_2. It rarely happens, however, that the CO_2 content in the cooled chimney gases from a coal-fired furnace exceeds 13·0 p.c., and the more usual proportion is from 8·0 to 10·0 p.c. In large boiler installations, the adoption of mechanical stoking, together with automatic instruments for recording the temperature and CO_2 content of the chimney gases, will be found conducive to fuel economy. E. J. Constam and P. Schläpfer of the Zurich Prüfungsanstalt für Brennstoff, as the result of exhaustive boiler trials with many different coals, conclude that those yielding between 16 and 23 p.c. of 'volatiles' (referred to dry ashless fuel) have the greatest steam-raising values; with coals yielding a high percentage of 'volatiles,' there is an excessive loss on account of their incomplete combustion; whilst, on the other hand, with a coal low in 'volatiles,' and which, therefore, yields a large percentage of coke in the boiler furnace, a considerable excess of air must be used in order to maintain combustion at a rate sufficient to ensure rapid evaporation in the boiler, and this means an excessive loss in sensible heat of the chimney gases. In trials on a marine boiler with coals yielding between 16·5 and 19·1 p.c. 'volatiles,' evaporating about 3·6 lbs. of water per sq. ft. of heating surface per hour, between 73·7 and 75·1 p.c. of the heat of combustion of the fuel was transmitted to the water, about 20 p.c. was lost in the chimney gases (at 276°–303°), partly as sensible heat and partly as unburnt gases, another 3–3·4 p.c. was lost in the ashes, the balance representing radiation losses (Zeit. des Ver. deut. Ingenieure, 1909, 1857). In trials on a goods locomotive on the Furness Railway, fired with Yorkshire, Lancashire, Cumberland, Scotch, and Welsh coals, the average boiler efficiency reported was 74·5 p.c. for an average evaporation of 8·65 lbs. of water per sq. ft. of heating surface (Pettigrew, Jour. Iron and Steel Inst. 1903, ii. 206). In coal-fired Lancashire boilers the efficiency realised rarely exceeds 70 p.c., and is sometimes much lower.

Anthracite is the ultimate product of the conversion of vegetable matter into coal. Its average composition is 91·29 C, 2·91 H, 2·75 O+N, 3·05 ash. The percentage of N varies from 0·58 to 2·85; that of sulphur from 0·63 to 1·0. Anthracite is hard and brittle; it has a sub-metallic lustre, a conchoidal fracture, and a sp.gr. of 1·35–1·7. It burns with a smokeless flame. Some varieties (*e.g.* Welsh anthracites) decrepitate considerably, even when gradually heated. This property is not exhibited by the anthracites of Pennsylvania.

2. *Carbonised Fuels.*

Wood charcoal. When wood is heated to 200° without access of air, it remains unaltered, at 220° it becomes brown, and at 270°–300° it suffers decomposition, torrefied wood or *Rothholz* being formed. At 350° it is resolved into volatile products and a fixed residue of charcoal. Good charcoal produced at 350°–400° is porous, black, sonorous when struck, has a conchoidal fracture and a ligneous texture. It burns without smoke, and in separate pieces without flame. Its sp.gr., exclusive of pores, is 1·5–2; inclusive of pores, 0·2–0·35 in soft charcoal, and 0·35–0·5 in hard. Dry charcoal contains on an average 90 C, 3 H, and 7 O. After storing, it contains 70·45 C, 1·68 H, 13·1 O, 1 ash, 13·76 moisture and gases. The usual percentage of ash is 3–4. The carbonisation or dry distillation of the wood may be effected in the open air in circular piles or stacks (Meiler), provided with a yielding cover, in rectangular piles, in pits (the most primitive method), in kilns of brick or stone, or in iron retorts heated externally (method used in the manufacture of gunpowder and of pyroligneous acid). The yield of charcoal varies with the nature, age, and condition of the wood, and with the method of carbonisation, from 31 p.c. by volume (branch-wood of fir) to 80 (logs of the same). In Sweden, 67 p.c. of the volume of the wood was obtained in piles in which the wood was stacked vertically, and 75 when stacked horizontally. The yield by weight ranges from 15 to 28 p.c. The more slowly the charring is effected, the greater will be the yield of charcoal. Charcoal is an excellent fuel for metallurgical purposes on account of its low percentage of ash and its high calorific power.

Peat charcoal is very friable and porous, and consequently difficult to use in metallurgical operations. When sufficiently coherent, and when the percentage of P_2O_5 is low, it may be used in low, small furnaces. The carbonisation may be effected in open kilns, in pits, or in ovens in which the air for combustion passes from above downwards, or by external firing in closed vessels, in order to enable the volatile products of distillation to be collected. Peat

charcoal is easily kindled, and has a calorific power of 6500–7000 cals. It is not adapted for iron making, but may be used advantageously for gas furnaces, on account of the large size of the lumps, absence of clinker, and the fact that the ash readily falls through the bars.

Coke is the solid product of the carbonisation of coal. It varies considerably in external character. For metallurgical purposes, the best coke is compact, heavy, homogeneous, with bright light-grey surface. It contains, besides carbon and ash, small quantities of hydrogen (0·2–1·2 p.c.), oxygen (traces and up to 8 p.c.), nitrogen (0·4–1·5 p.c.), and 'organic' sulphur (total S=0·8–1·8 p.c.). The best cokes contain upwards of 90 p.c. C, and less than 8 p.c. ash, and should have a metallic ring. Coke is only slightly hygroscopic, and when thoroughly dried does not absorb more than 1–2 p.c. of moisture from moist air. The moisture in coke put on the market should not exceed 3 p.c. The calorific value of dry coke containing 90 p.c. C and 0·5 p.c. H is about 7450 K.C.U. per kilog. (cf. COKE MANUFACTURE).

Coalite (semi-coke). A smokeless fuel, for domestic use chiefly, prepared by carbonising a gas coal at low temperature (425°) in narrow vertical retorts heated by producer gas. On a plant erected at the Plymouth Gasworks in three units, it has been stated that each unit will produce 35 tons of 'coalite,' and 280,000 cub. ft. of 20 p.c. gas from 56 tons of coal per diem, the carbonising period being 3½ hours per charge. The fuel consumption is said to be as low as 6 p.c. of the coal treated, and it is claimed that the tar oils obtained are of considerable value.

3. *Compressed Fuels.*

Patent fuel (briquettes). Numerous patents have been taken out for producing a good fuel by mixing various substances with small coal in proportions sufficient to enable the mixture to be pressed into a coherent block. Various binding materials have been tried, *e.g.* soluble glass, asphalt, turpentine. Meal made from potatos was abandoned because the blocks were not water-tight. Coal tar (Warlick's process) was tried at Swansea, the blocks being baked after compression, whereby a quantity of tar was recovered. On the Continent, cellulose (D. R. P. 7590, 1879) and treacle (D. R. P. 31715, 1884) have been tried. Pitch made from coal tar has been used for many years with great success. Two modes of manufacture are in vogue in South Wales. In the dry process, small coal is carried by an elevator into a large bunker, whence it is lifted by another elevator to a shoot into which it is tipped with the contents of a small elevator containing pitch. The mixture then passes into a Carr's disintegrator, and the resulting product, containing 8–12 p.c. of pitch, passes to heaters, and finally to the presses, which turn out 100–200 blocks, weighing 10–30 lbs. per day of 12 hours. In the steam process, there is used a large vertical iron cylinder with arms revolving inside, constantly kept full of the mixture of pitch and coal. High-pressure steam is injected near the bottom, and allowed to percolate up through the mass, whilst the arms expose every portion to its action. Attempts have been made to utilise peat by mixing it in a state of powder with small coal and sawdust, and pressing the mixture into blocks. According to tests carried out by the staff of the U.S. Geol. Survey in 1904, it is possible to make good briquettes from a strongly coking coal, heated until intumescence just begins, and immediately afterwards pressed, without the addition of any binding agent. Anthracite culm or coke breeze may be briquetted without the addition of any bituminous coal, provided that good pitch be used as a binding agent. The pitch should be anhydrous, or nearly so, and should contain a certain proportion (7–14 p.c.) of creosote oils distilling below 215°, to give it good binding properties; a good quality of powdered coal with 6 p.c. of pitch should yield a clean hard briquette, which will not disintegrate in the fire. In many cases briquetted coal will stand transportation better than the original coal, and is as good or even better as a steam-raising fuel.

Literature.—E. Preissig, Presskohlenindustrie, Freiberg, 1887; Report of Coal Testing Plant of U.S. Geol. Survey, iii. 1904.

4. *Powdered Fuels.*

In the system of burning powdered fuel worked out by Crampton (J. Iron and Steel Inst. 1873, 91), the coal is pulverised until it passes through a 30-sieve, and fed into the furnace by a kind of injector, air being supplied in measured quantities by a fan, so that intense heat is generated. This method has been successful as regards economy and regularity of high temperature. (On powdered fuel, consult Isherwood, Proc. Inst. C.E. 44, 289; W. G. McMillan, J. Soc. Arts, 34, 527.)

Valuation of coals. Whilst the value of coal as a fuel depends primarily upon its calorific value, other factors must be considered in determining its suitability for any given purpose, as, for instance, (1) moisture content; (2) quantity and fusibility of ash; (3) percentage of 'volatiles' and the character of the coke residue; (4) ultimate analysis—C, H, S, and N,—the N being important if the coal is to be carbonised or gasified in producers under ammonia-recovery conditions. Coal is rarely purchased in Great Britain subject to either chemical analysis or calorific test, but the practice is common in the United States and in certain European countries, the contract, in any particular case, naming a certain price for a coal of specified quality, subject to a sliding scale for variations in quality within certain defined limits. In sampling a consignment of coal for assay purposes, special care should be taken that the sample truly represents the bulk; the method adopted will obviously depend somewhat on circumstances, but the sample should contain the same proportions of large, medium, and small coal as the bulk, and, as a rule, should weigh not less than 1 cwt. On reaching the laboratory the whole should be put through a crusher and subsequently reduced to convenient bulk by successive 'quartering'; the final sample should then be further crushed to coarse powder and stored away in air-tight tins. The chemical tests may be carried out as follows: (1) *Moisture and ash.* 10 grams of sample, in a weighed porcelain basin, are dried in an oven at 105° for 1 hour, and subsequently incinerated in a muffle at bright red heat, care being taken that

the initial 'distillation' is not too rapid. The colour of the ash should be recorded, and observation made as to its fusibility. (2) *Volatile matter.* The method recommended by a committee of the American Chemical Society is to determine loss in weight when 1 gram of the dry sample is heated in a covered platinum crucible of 30 c.c. capacity for 7 minutes over the full flame of a Bunsen burner, screened from draughts by a cylindrical asbestos chimney. A more useful test, however, is the 'crucible coke assay,' in which 20 grams of the dried sample are carbonised in a fire-clay crucible (lid on) at 900°–1000° in a muffle furnace; the heating is continued for 5–10 minutes after the flame, caused by the volatile matter burning at small holes in the crucible lid, has completely died away. If comparative tests are made always at the same temperature, the method is of great practical value, inasmuch as it allows of the character of the coke residue to be properly judged. (3) *Ultimate analysis for C and H.* This may be carried out on a dried sample (0·2 gram) by the 'combustion' method ordinarily employed in the case of organic compounds, the combustion tube being packed with granular lead chromate. (4) *Sulphur.* 1 gram of the sample is intimately mixed in a platinum crucible or dish with 1 gram of pure calcined magnesia and 0·5 gram dry Na_2CO_3 (free from sulphate) by means of a stout platinum wire. The vessel is then cautiously heated by means of an alcohol lamp, the mass being constantly heated until vivid glowing has ceased; the temperature is then raised until the bottom of the vessel is at full red heat and the carbon burned away. If there is difficulty in completely burning off the carbon, the vessel should be cooled, a small quantity of powdered ammonium nitrate well mixed with the residue, and the incineration continued (lid on). Finally, the residue is transferred to a beaker, and the vessel washed out with about 50 c.c. water. The liquid is boiled for 5 minutes with 15 c.c. of saturated bromine water; the insoluble residue is allowed to settle, and, after decantation of the supernatant liquid, is boiled a second and a third time with 30 c.c. of water. The filtrate is subsequently acidified with HCl, boiled to expel the bromine, and the sulphate precipitated with 10 c.c. of 10 p.c. $BaCl_2$ solution. If the coal contains much FeS_2 or $CaSO_4$, the residual MgO should be dissolved in hydrochloric acid, and the solution tested for sulphate. (5) *Nitrogen* is best determined by the ordinary Kjeldahl method. Occasionally coal or coke must be examined for *arsenic.* (For details of the method recommended by the committee appointed by the Board of Inland Revenue, *see* T. E. Thorpe, Estimation of Arsenic in Fuel (Chem. Soc. Trans. 1903, 83, 969).)

Storage and spontaneous ignition of coal. It is well known that on storage coal deteriorates both as regards heating power and coking properties, a fact attributable to slow atmospheric oxidation, which may, in certain circumstances, give rise to spontaneous ignition of the coal. It was formerly believed that the oxidation of the iron pyrites present in coal is the principal cause of its spontaneous ignition, but it is now recognised that this is not so, the chief factor being the surface condensation of oxygen in the pores of the fuel, and subsequent oxidation of certain constituents of the coal substance. It has also been suggested, on the basis of experimental evidence, that in some cases of spontaneous combustion, the heat generated by bacterial activity is a factor to be considered. Coal readily absorbs oxygen when heated in contact with air at 150°–200°, the process being not merely a physical absorption, but involving actual oxidation of coal substance; the weight first of all increases, and afterwards, especially if the temperature rises, steadily decreases owing to loss of moisture, slow combustion, and decomposition. According to investigations by S. W. Parr and F. W. Cressman, of the University of Illinois, the oxidation of coal is continuous over a wide range of conditions, and begins with freshly mined coal at ordinary temperatures; at some temperatures between 200° and 275° (dependent upon the nature of the coal and the fineness of division) the oxidation becomes autogenous; actual ignition does not occur until the temperature rises beyond 350°. It has been proved that coal stored *under water* suffers no deterioration. The conditions most favourable to spontaneous ignition of coal are (1) a certain, but not excessive, ventilation of the heap; (2) a certain degree of subdivision (*e.g.* small coal mixed with dust); and (3) any circumstance which tends to heat conservation in the heap. The best safeguard is either excessive ventilation (which it is practically impossible to maintain in large stores or in a ship's hold) or no ventilation at all. The extinction of fires which may break out on board ship is often a matter of great difficulty, the most effective method being that recently proposed by Harker, whereby the flue gases from the boilers of the vessel are pumped into the burning hold.

British coal-fields. The coal-fields of Great Britain may be grouped in three principal areas, each having distinctive features, namely: (*a*) *Southern* (S. Wales, Forest of Dean, Somerset, and Dover); (*b*) *Central* (Yorkshire, Lancashire, Derbyshire, N. Wales, and Midland Counties); and (c) *Northern* (Scotland, Northumberland, Durham, and Cumberland). The more important fields are as follows:—

(1) *South Wales* (Monmouth, Glamorgan, Carmarthen, and Pembrokeshire), covering an area of 1000 sq. miles, of which 153 are under the sea, with seams 1–12 feet (average 2·5–3·0 feet) thick, and yielding all classes of coal, bituminous (31 p.c.), steam coals (47 p.c.), and anthracites (22 p.c.). Speaking generally, and for corresponding depths below the surface, there is a gradual transition in the character of the coal from the coking varieties in the east, through the first-class steam coals of the centre, to the semi-anthracites and anthracites in the west; moreover, the seams have apparently been subjected to an increasing earth pressure in the direction east to west, a circumstance which may account for their increasing anthracitic character; this supposition has been disputed by Strahan and Pollard (Memoirs of the Geological Survey, 1908), who, from the fact that the ash content of the anthracites is invariably much lower than that of the neighbouring bituminous seams, argue that the difference between the two classes of coals must be

due to some difference in the original vegetable *débris* from which they have been derived. In the east section of the field the upper and middle coal-measures are worked, yielding good coking and bituminous coals; in the centre the middle measures predominate, the upper being found in patches only; whilst in the extreme west the lower measures only are found. The composition of the more important classes of coals usually falls within the following limits:—

Class	C	H	O and N	S	Ash	Volatiles
Anthracites . .	91·0–93·0	3·0–3·7	1·9–3·5	0·7–1·0	0·7–1·7	5·0–6·0
Steam . . .	85·0–90·0	4·0–4·7	3·5–4·5	0·7–1·5	2·0–3·3	7·0–20·0
Bituminous (coking)	80·0–95·0	5·0–5·5	—	—	—	20·0–25·0

(2) *Forest of Dean.* A small field (34 sq. miles) between the Wye and Severn valleys, containing 31 seams, of which only 16 exceed 1 foot in thickness; the upper, middle, and lower measures cover practically the whole area, except where the basin comes to the surface, when the lower only occur; the coals resemble in character those found in the east section of the S. Wales field; the upper and middle measures yield excellent gas and house coals, and the lower measures, which, however, are difficult to work, owing to accumulation of water therein, contain good steam coals. (3) *Bristol.* Generally speaking, the upper, middle, and lower measures are found, and the seams are of greater total thickness than in either S. Wales or the Forest of Dean; both gas and house coals of poor coking qualities are obtained. (4) *Staffordshire,* divided into N. Staffs. (95 sq. miles) and S. Staffs. (150 sq. miles). In the northern area the sequence of upper, middle, and lower measures is complete, although much broken by faults; towards the south the measures thin out considerably in respect of total thickness, but the individual seams converge, finally forming the famous Dudley 10-yards seam; in the extreme south the lower measures become so attenuated that it is doubtful whether they exist at all. The northern area yields good coking as well as gas, house, and furnace coals; in the south coking and steam coals are practically non-existent, but both gas and house coals (chiefly of the Pennant series) are obtained. (5) *Leicestershire* and *Warwickshire.* In Leicestershire the exposed area is about 30 sq. miles, and in Warwickshire about 150 sq. miles; the seams have been subjected to igneous intrusion, and probably also to atmospheric influences, and are generally 'oxidised'; hence the coals are non-coking, with a high percentage of 'volatiles.' (6) *Yorkshire, Derbyshire, and Nottingham.* A large area, including some 3900 sq. miles of 'concealed,' and about 1300 sq. miles of 'exposed' measures; the upper measures have been proved in boring operations, but they are very thin and of no commercial importance. The chief seams belong to the Pennant (middle) series; all seams yield highly bituminous coals, with 25–40 p.c. 'volatiles.' The best house coals are obtained in this field. All the coals found north of Sheffield have marked coking properties, though few of them yield a really first-class coke; south of Sheffield the character of the coal changes, gradually losing its coking properties. Between Mansfield and Nottingham the seams have been 'oxidised,' and although the coal yields a large amount of gas, it is non-coking. (7) *Lancashire.* An irregular area, much faulted, extending from Burnley in the north to Ashton-on-Lyne in the south (with a long tongue projecting southwards through Stockport to Macclesfield), and from Oldham in the east to St. Helens in the west. Total 'exposed' area=217 sq. miles. The principal seams are in the Pennant (middle) series; the upper measures contain no workable seams, but the lower measures become important in the Accrington and Burnley districts. The coals from the Pennant series belong almost exclusively to the 'gas-coal' class, containing 30–35 p.c. 'volatiles'; several of the seams, notably the Yard Mine, Arley, and Trencherbone, yield a fairly good coking coal; the famous 'Mountain Mine' seams of the lower measures (Burnley and Accrington) yield a coal with 26–27 p.c. 'volatiles,' which produce a coke almost, if not quite, equal to the best Durham coke. (8) *North Wales* (Flints. and Denbighs.). Similar in character to the Lancashire field, but with the upper measures rather more developed. The principal seams are in the Pennant series; the seams in the lower measure are all thin. The coals are similar to those of Lancashire; they contain 33–35 p.c. 'volatiles,' and yield a fair quality of coke. (9) *Durham and Northumberland.* In the great northern coal-field, of which Durham and Northumberland form a part, there is a development of coal-seams (more strongly marked the farther north) in the Carboniferous limestone, a feature which is absent in the Midland and Southern fields. Opinion is divided as to the existence of the upper measures in Durham and Northumberland; the middle measures are well developed; the lower measures are thin. In the limestone there are a few workable seams which increase in number and thickness from south to north. The total area of the coal-field is 800 sq. miles. The S. and W. districts of Durham produce, perhaps, the finest coking coals in the world, containing 22–28 p.c. 'volatiles,' and low both in sulphur and ash. The central district (Sunderland to Newcastle) produces fine qualities of gas and house coals. The Northumberland seams are, for the most part, 'oxidised'; they contain a rather large amount of moisture, and are non-coking. They are largely used as steam coals, and they are excellent as 'producer' coals. (10) *Cumberland.* The character of the coals is similar to those obtained in N. Durham. (11) *Scotland.* The Scottish coal-fields extend from Fifeshire on the east, across a belt between the Forth and Clyde, and westwards into Lanarkshire and Ayrshire, with an isolated small area in Midlothian. The upper measures are well developed throughout the area; the middle (Pennant) measures are practically non-existent,

whilst the lower measures attain a thickness of 800–1500 feet. Below the latter is the '*edge-coal*' series in the Carboniferous limestone, highly inclined to the horizontal (Fifeshire, Midlothian), and containing bands of cannel. Generally speaking, the coals are bituminous, with a high percentage of 'volatiles'; the best coking varieties are found in the neighbourhood of Glasgow, and the coking seams stretch as far eastward as the Firth of Forth. The Ayrshire coals are chiefly non-coking, and are excellent as 'producer' coals. In Fifeshire the seams in the Carboniferous limestone in the neighbourhood of Dunfermline yield first-class steam and house coals. The Scottish coal-fields have been subjected to igneous intrusions to an extent rarely met with in England, and, consequently, some of the bituminous seams have been locally converted into steam coals and anthracitic varieties.

German coal-fields. The principal German coal-fields are those of (1) *Upper Silesia* (districts of Ratibor, Beuthen, Zabrze, Konigshütte, Laurahütte, and Pless). The measures are 600 metres deep with seams 3–4 metres thick. The best coking coals are found near Zabrze eastwards, from which they gradually change into young gas coals, near Konigshütte, and finally into non-coking flaming coals near Laurahütte. (2) The *Ruhr basin*, stretching from the neighbourhood of Hamm in the N.E. to the Rhine in the S.W.; the field is much broken by faults, and the older measures, which yield the best coking coals, are, as a rule, uppermost; the middle measures yield gas coals, and the lower measures non-coking varieties. The coals of the Ruhr basin contain 84–97 p.c. of organic matter, of which C=83·1–87·1, and H=5·27–5·68. (3) The *Saar district*; the upper and middle measures are both thin and yield non-coking and flaming coals, the lower measures are thick, and yield (especially the deepest) very good caking and coking coals. The ash in Saar coals varies between 1·5 and 4·5 p.c. as a rule, occasionally running up to 7·7 p.c. The carbon varies between 70 and 84 p.c., and the hydrogen between 4·7 and 5·2 p.c.

American coal-fields. The following information has been abstracted from the comprehensive Report of the U.S. Geological Survey issued in 1906; the chief coal-producing states are arranged in order of their present economic importance, the figures in brackets indicating in each case the output in millions of short tons, for 1904. (1) *Pennsylvania* (73·1 anthracitic and 98 bituminous). The anthracite field lies in the N.E. and the bituminous field in the W.; the latter produces the famous Connellsville coking coals, the almost equally famous Yonghiogheny gas coals, and numerous grades of steam and domestic coals. (2) *Illinois* (36·5). This state includes the greater part of the eastern interior coal-field, which extends from Rock Island and Wilmington (Ill.) in the north to Central Kentucky in the south and from the Mississippi river in the west to Williamsport and Cannelton (Ind.) in the east. The coals are rather low grade and weakly coking, containing C=54–76, H=4·5–5·3, N=0·8–1·2, S=1·3–4·5, O = 12·0–18·5, and ash = 12·0–24·0 with calorific values 9929–11,907 B.Th.Us. per lb. The proximity of the field to Chicago and St. Louis enhances its economic importance. (3) *West Virginia* (32·6). This state includes a large portion of the important Central Appalachian coal-field, which produces high-grade steam coals also suitable for coking purposes, and containing C=74–86, H=4·0–5·2, N=1·0–1·7, S=0·5–1·2, ash=4·6–11·3, with calorific value 13,736–15,190 B.Th.Us. per lb. (4) *Alabama* (11·26) includes several fields of which the Warrior basin is the most important (23 workable seams), constituting the fuel supply of the Birmingham (Ala.) iron industry. The coal is of fair coking quality, containing C=69–72, H=4·8–5·0, N=1·55–1·66, S=0·7–1·02, ash=12·5–12·6, with calorific value 12,238–12,992 B.Th.Us. per lb. (5) *Indiana* (10·9) includes the eastern section of the Eastern interior coal-field (*vide* Illinois). (6) *Kentucky* (7·5). The eastern part of the state includes part of the Central Appalachian coal-field (*vide* West Virginia) and part of the eastern interior field in the west. Both fields yield good steam and coking coals, the eastern area being in this respect superior to the western; the coke for the western field has too high a S content to be of much use as a metallurgical fuel. (7) *Colorado* (6·65). The most important coal-producing state west of the Mississippi river; the coal is a black lignite, which so rapidly disintegrates on exposure to air, that its transport over any great distance is impossible. It contains C=61·1, H=5·75, N=1·22, S=0·58, O=24·95, ash=6·37, with cal. value 10,546 B.Th.Us. per lb. (8) *Iowa* (6·5) yields only low-grade coals containing high percentages of moisture, sulphur, and ash, with very feeble coking properties. (9) *Kansas* (6·3) yields fairly good non-coking steam coals. (10) *Wyoming* (5·1) contains a number of apparently independent coal-fields in strata of the Cretaceous age; the fuel is low grade. (11) *Indian Territory* (3·04) produces good steam coal, with, in some instances, fair coking properties, but usually high in sulphur. C=63–72, H=4·8–5·2, N=1·4–1·7, S=1·5–4·0, ash=10·0–13·5, with cal. value 11,340–12,874 B.Th.Us. per lb. The coke is good enough for lead smelting, but unsuitable for iron smelting.

Literature.—Fleck und Hartig, Technik der Steinkohls, München, 1865; J. Percy, Metallurgy; Fuel, 155–577, 2nd ed. London, 1875; E. J. Mills and F. D. Rowan, Fuel and its Application, London, 1889; Frech, Ergiebigkiet der Steinkohlenlager, Stuttgart, 1901; Wedding, Eisenhuttenkunde, Bd. ii. Braunschwig, 1902; W. Carrick Anderson, Chemistry of Coke, Glasgow and Edinburgh, 1904; Report of Royal Commission on Coal Supplies, London, 1905; Report on the Coal-testing Plant of the U.S. Geological Survey, pts. i.–iii. Washington, 1906; Gibson, Geology of Coal and Coal-mining, London, 1908; Greenwell and Elsden, Analyses of British Coals and Coke, 3rd ed. London, 1909; Franke, Handbuch der Brikettirung, Stuttgart, 1909.

B. Liquid Fuels.

Whilst increasing quantities of hydrocarbon oils (crude petroleum or its distillation products, shale oil, benzol, &c.) are being used as fuel for certain special purposes, they cannot be regarded as a serious competitor of coal or as in any real sense a substitute for it; it is doubtful whether the calorific value of the world's entire output of petroleum and other liquid fuels in

any given year exceeds (if, indeed, it is equal to) 5 p.c. of that of the corresponding output of coal. Nevertheless, there are certain selected purposes (*e.g.* for motor-car engines and the like) for which volatile hydrocarbon oils are employed without displacing coal or gaseous fuels, and other special cases, notably steam raising in ships of war, in which liquid fuel has important advantages over coal. In respect of naval requirements, these are principally (i.) economy of space and ease in replenishing supplies; (ii.) ready and immediate response to varying loads; (iii.) possibility of forcing boiler to extreme duty in case of emergency; (iv.) absence of smoke under normal working conditions; (v.) shortness of chimney stack; (vi.) abolition of stoking; and (vii.) ability to secure and maintain higher speeds than with coal firing. Some of these advantages are also of value in relation to locomotive-boiler firing, especially in countries (United States, Russia) where petroleum is abundant. In the Report issued by the U.S. 'Liquid Fuel' Board in 1904, the relative all-round efficiencies of oil and good steaming coal, from the naval point of view, are estimated to be as 18 : 10, whilst Mr. James Holden, locomotive superintendent of the G.E.R., in giving evidence before the Royal Commission on Coal Supplies, stated that, according to his experience, petroleum fuel oil had, weight for weight, approx. twice the steam-raising power of coal in locomotive boilers. The latter estimate is probably based on the best rather than on the average results obtained with oil fuel, but certainly the ratio is not less than 3 : 2. Moreover, weight for weight, oil occupies much less space than coal, whilst oil does not deteriorate on long keeping as does coal.

Petroleum fuel oil (*see also* PETROLEUM). About 63 p.c. of the world's total supplies of petroleum are drawn from the United States (California, Kansas, Indian Territory, Oklahoma, Ohio, Texas, Pennsylvania, Virginia, Louisiana, and Illinois), and a further 25 p.c. from Russia (mainly the Baku oil-field); the remaining 12 p.c. is chiefly derived from Roumania, Galicia, India, and the Eastern Archipelago. The total annual output probably amounts to about 1000 million imperial gallons. Crude petroleum, in its natural state, often contains a certain amount of water in emulsified form, and also of volatile hydrocarbons. The oil should be both dehydrated and freed from volatile constituents before it can be safely transported, stored, and used as fuel. In Germany and for the British mercantile marine, the prescribed minimum flash-point for fuel oil is 150°F. (Abel test), whilst the British Admiralty require a minimum of 200°F. for warship fuel. A good fuel oil should also be sufficiently free from solid hydrocarbons to stand a temperature of 0° without solidification.

The appearance of crude fuel oil, as put on the market, varies greatly, according to its origin; some varieties have a pale colour and are mobile, others are viscous and almost black in colour. Sp.gr. varies between 0·771 and 1·06; American oil has sp.gr. 0·785–0·936; Baku oil, 0·854–0·899; Galician oil, 0·799–0·902. Whilst consisting essentially of hydrocarbons, crude oils contain small but variable percentages of N, S, and O. The nitrogen (0·25–1·0 p.c.) is present in the form of basic substances, probably of the pyridine or quinoline type; sulphur (0·5–1·5 p.c.) occurs both as alkyl sulphides (American oils) and as thiophen compounds (European oils). The following gives the ultimate composition of various crude oils:—

Origin	C	H	N	S	O	Sp.gr
California	84·43	10·99	0·65	0·59	3·34	0·962
Texas .	84·60	10·90	—	1·63	2·87	—
„ .	85·75	12·75	—	1·47	—	—
Java .	87·1	12·0	—	—	—	0·923
Baku .	85·3	11·6	—	—	—	0·940

Of the hydrocarbon constituents, members of the following series are known to be present in petroleum: C_nH_{2n+2} *paraffin*, C_nH_{2n} *naphthenes*, and C_nH_{2n-2} . . . C_nH_{2n-12}. Mendelejéff has concluded that all crude oils contain the same classes of hydrocarbons, but in widely different proportions. Pennsylvanian oil consists chiefly of the C_nH_{2n+2} series; Californian oil chiefly of the C_nH_{2n} (naphthene) series, together with some benzene and its homologues; Texas oil, which is dark in colour and viscous, contains principally members of the C_nH_{2n-2} and C_nH_{2n-4} series; naphthenes C_nH_{2n}, constitute 80 p.c. of Baku oil. Of hydrocarbons, such as naphthalene, acenaphthalene, fluorene, anthracene, and phenanthrene, all of which are found in coal tar, the only one undoubtedly present in crude petroleum is naphthalene. The gross calorific value of petroleum fuel oil varies, as a rule, between 10,350 and 11,000 K.C.Us. per kilog.; the natural oils best adapted for fuel purposes are those derived from California, Texas, Mexico, and Borneo. In Russia, where a great oil-fuel industry has been developed, the residue ('astatki') after distilling off the kerosene and burning oil, is used. In applying oil to boiler and furnace work generally, the fuel must be '*atomised*' by means of a jet of high-pressure steam or compressed air in a special form of burner working on the 'injector' principle. The oil should enter the furnace as a fine spray, intimately mixed with the air requisite for its combustion. Many forms of such burners are on the market. From the chemical aspect of combustion of the oil, the use of compressed air is preferable to steam as the 'atomising' agent, although, in fact, steam is more usually employed. In other forms of burners, the 'atomising' is effected, without either air or steam, simply by forcing the oil (preheated to 130°) under considerable pressure (50 lbs. per sq. inch) through a suitable orifice.

The following typical burners may be quoted as examples: (*a*) the 'Carbogen' burner (Fig. 1), which may be used with either

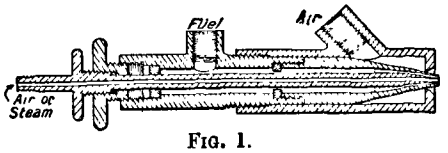


FIG. 1.

steam or compressed air as the atomising agent: (*b*) the 'Kermode' hot-air burner (Fig. 2), in which the oil is partially vapourised and sprayed

by means of hot air at a pressure of from ½ to 4 lbs. per sq. inch. The oil enters at A, its further flow being regulated by a conical valve and slit. The air, suitably preheated, enters at the branches B and C; the portion passing through C meets the oil as it passes the oil-control valve, which is regulated by the wheel E, and both travel on together through the central

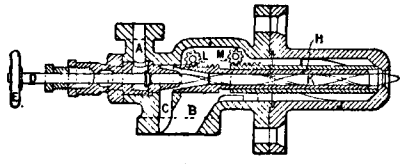


FIG. 2.

tube K, in which is fixed a helix, whereby complete mixture of oil vapour and air is ensured. The two air supplies, through B and C, are separately controlled by means of the rack and pinion at M and L respectively: and (*c*) the 'Kermode' pressure jet burner (Fig. 3), in which a supply of oil pumped into the burner through the side tube A, and passing thence through the narrow annulus D, is 'atomised' by being forced through a series of narrow grooves cut in the plug

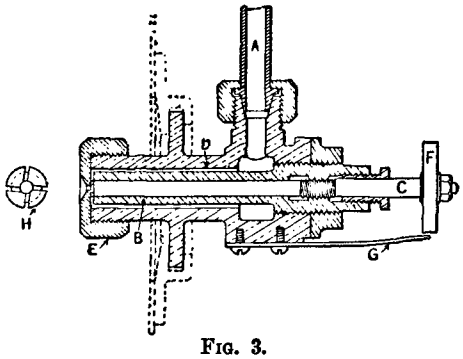


FIG. 3.

end of B, parallel to the centre line of the burner, whilst similar grooves are cut in the face of B at right angles to the axis of the burner. The grooves, as shown in H, are tangential to the cone end of the spindle C, which regulates the size of the available opening through the cap nut E. A separate forced or induced air draught is used with this burner. (*d*) A type of burner designed by Messrs. John Burden and Sons, of Bellshill near Glasgow, in which an air-injected oil spray is completely gasified and mixed with air before ignition by passage through a heated iron tube, by which means a perfectly non-luminous 'bunsen' flame of great calorific intensity is obtained.

The furnace in which the 'atomised' oil is burnt should be so constructed that the flame does not come into direct contact with cold metallic surfaces. An incandescent solid surface greatly assists the completion of combustion and prevents smoke formation. (For various forms of burners, boiler-furnaces, and the like, *v.* W. H. Booth, Liquid Fuel and its Combustion, 118–221; also Redwood's Petroleum, ii. 705–714.)

Petroleum oils are also employed as fuel in internal-combustion engines. With all the earlier forms of petroleum engines, as with the modern motor-car engine, it was necessary to employ a light petroleum spirit ('petrol'), but in modern types of stationary engines, kerosene and even unrefined oils of higher boiling-points may be used. These engines usually work on the four-cycle principle. A charge of vapourised oil and air is drawn into the cylinder on the out-stroke of the piston: on the return stroke it is compressed and fired by a spark at the inner dead point. The piston is then propelled outwards by the explosion, and on the return stroke the products are expelled. Part of the heat of the products is utilised in vapourising the oil or heating the air, or both. According to trials made for the Royal Agricultural Society in 1901 by Professor Ewing, the oil consumption (American kerosene, sp.gr. 0·801, flash-point 86°F., and cal. value 10,329 K.C.Us. per kilog.) on 5 types of engines, developing 6 to 15 b.h.p., varied between 0·69 and 1·30 lb. per b.h.p.-hour. The highest thermal efficiency indicated by these trials was 20 p.c. The Diesel oil engine, which has a higher thermal efficiency than any other heat engine, burns ordinary unrefined fuel oil; the cycle consists of four strokes, namely, (1) out-stroke, in which air at atmospheric pressure is drawn into the cylinder; (2) compression stroke, in which the air is compressed to about 35–40 atmospheres, thereby becoming highly heated,—when the compression has reached about 10 atmospheres, part of the air is drawn out by a single-acting air pump and forced into a receiver (which is in direct communication with the admission valve chamber) at a pressure of about 47 atmospheres; (3) out-stroke, during the initial part of which oil, previously forced into the admission valve chamber, is sprayed into the cylinder by a small quantity of the highly compressed air in the receiver. The oil immediately burns in the hot compressed air in the cylinder, no sparking or other similar ignition device being required to start the combustion; the products of combustion then expand,—this is the working stroke; and (4) return stroke, the products are expelled from the cylinder. The makers of the engine guarantee that the consumption of crude petroleum will not be more than 0·452 lb. per b.h.p. per hour at full load, equivalent to a thermal efficiency of 35 p.c. Exhaustive trials by Mr. Ade Clark (Proc. Inst. Mech. Eng. 1903) on a two-cylinder 160 h.p. engine at Ghent, showed a thermal efficiency at full load of 32·3 p.c. per b.h.p.-hour, on a single-cylinder 80 h.p. engine, the corresponding efficiency was 31·2 p.c. The Diesel Engine Co. have produced a marine type of engine which can be coupled direct to the propeller shaft without the intervention of a clutch or other similar gear. The engine is reversible, and its speed is variable at will. Successful trials have been made with coal tar as fuel for the Diesel engine.

Literature.—Redwood, Petroleum (2 vols.), and W. H. Booth, Liquid Fuel and its Combustion.

C. GASEOUS FUELS.

The great advantage of gaseous over solid or liquid fuels, for heating purposes, lies in the fact that they can be completely burned in furnaces of regenerative type with only a slight excess of

air, and they are therefore specially adapted for purposes where very high temperatures on a large scale are required. The absence of smoke and ash makes their extended use, from the public point of view, eminently desirable; moreover, the possibility of gasifying coal under ammonia-recovery conditions, coupled with the much higher thermal efficiency of an internal-combustion engine as compared with a steam engine or turbine, has firmly established the position of gaseous fuels in relation to power schemes.

Natural gas. In the petroleum districts of Pennsylvania and adjoining states, natural gas issues from the strata at a depth of 500–2000 feet below the surface, and when bore holes are sunk into this accumulation, the gas rises under a mean pressure of 250–400 lbs. per sq. inch. Between the years 1821 and 1883 natural gas had been used in a limited way for illuminating and heating purposes; since 1883, however, it has undergone an extraordinarily rapid development for industrial purposes. According to the Report of the British Iron Trade Association Commission to the United States (1902), the companies engaged in the natural-gas business in the Pittsburg district were operating nearly 3000 miles of pipe lines, and the daily consumption of gas throughout the year averaged about 130 million cub. ft., and in the winter time was 50 p.c. greater. Two companies bring gas from a distance of more than 100 miles. In 1907 the total consumption of natural gas in the U.S. (about half of which was in Pennsylvania) was 400,000 million cub. ft., the fuel value of which was computed at 50 million dollars. The composition of the gas varies in different wells, and even in the same well after a short lapse of time; methane (64–94 p.c.) is its principal constituent; hydrogen (3–30 p.c.), together with small percentages of ethane, ethylene, carbon monoxide, and nitrogen make up the balance. The density varies between 0·45 and 0·55. Natural gas has never been found in Great Britain except in too small quantity to be industrially important; in 1895 gas was encountered during well-sinking operations at Heathfield (Sussex), at a depth of 300 feet. In 1902 gas was issuing from the bore holes at a pressure of 140–200 lbs. per sq. inch; it contained 93·16 CH_4, 2·94 C_2H_6, 1·00 CO, and 2·9 p.c. N_2, but no hydrogen.

Coal gas (coke-oven gas). Gas manufactured by the carbonisation of bituminous coals in retorts, freed from tar, NH_3, and H_2S, and in some instances mixed with either blue or carburetted water gas, constitutes the chief public gas supply throughout the world. Within recent years the surplus gas from by-product coking plants has been purified for public use, and in localities where metallurgical coke is largely prepared, 'coke-oven gas' will probably be more extensively used in the future. The composition of coal gas varies considerably in different localities, according to the nature of the coal, the nature and disposition of the retorts, and the temperature of carbonisation. A good coal gas should contain 45–50 H_2, 30–35 CH_4, 4·0 heavy hydrocarbons (reckoned as C_2H_4), 5·0–10·0 CO, together with not more than 5·0 p.c. N_2; and should have a cal. value not less than 575 net and 645 gross B.Th.Us. per cub. ft. at 0° and 760 mm. The cost of manufacturing and distributing the gas (it being rarely supplied to the consumer for less than 2*s.* per 1000 cub. ft.) prohibits its use as a manufacturing fuel, except for small scale operations, but as a domestic fuel it has many advantages over raw coal. Tests carried out in the Fuel Department of Leeds University have shown that a well-constituted modern gas fire, in which the columnar fire-clay 'radiant' material is properly disposed in relation to the atmospheric burners, will not only completely burn the gas without a vestige of carbon monoxide escaping into the room, but it has an unexpectedly high 'radiation' efficiency. The total '*radiation*' from such a fire will vary from 30 to 35 p.c., whilst about 30 p.c. of the heat generated passes directly into the flue, the balance being 'convected' into the room (Reports of the Gas-heating Research Committee, Trans. Inst. of Gas Engineers, 1909, 59–101; 1910, 156–210).

Large surpluses of 'coke-oven gas,' which is little, if at all, inferior to many town gas supplies, are now available for steam raising or as gas-engine fuel. The efficiency of the gas when burnt in Lancashire boilers rarely exceeds 65–70 p.c., and with coal at 10*s.* per ton the cost of the gas for steam raising does not exceed 3*d.* per 1000 cub. ft. With the rapid extension of by-product coking plants in Great Britain, the proper utilisation of the energy represented by the surplus gas is becoming a problem of national importance.

Producer gas. For the cheap and rapid production of gaseous fuel for industrial purposes, there is no better process than the gasification of solid fuels (peat, bituminous coal, coke, or anthracite) by means of a mixed air-steam blast (sometimes air alone is employed) in some form of gas 'producer,' whereby the fuel is converted into gas containing some 35–45 p.c. of combustible constituents (CO, H, and CH_4). A modern gas producer consists of a cylindrical furnace, 6–12 feet internal diameter and 10–15 feet high, lined with fire-brick with an outer mild steel casing, and usually water-sealed at the bottom. Means are provided (1) for the introduction of the blast through some form of grate or twyer fixed immediately above the level of the water in the seal, and its regular distribution through the bed of incandescent fuel (usually 3–5 feet in thickness) which rests upon a lower bed of ashes; and (2) for the charging in of the raw fuel through (usually) some form of bell hopper fixed centrally on the top of the producer, round which are arranged a number of equidistant poking holes closed by iron balls. The gas outlet is fixed near the top of the cylindrical furnace. Taking as a typical example a producer working with a mixed air-steam blast on a common bituminous coal, the chemistry of gasification may be epitomised as follows. When a fresh charge of fuel is dropped into the furnace, it first of all undergoes a process of distillation on the top of the fire, whereby H, CH_4, tarry hydrocarbons, CO, together with small quantities of NH_3, H_2S, &c., are evolved, probably in much the same proportions as in the ordinary retort distillation of coal; olefines and higher paraffins are, however, so rapidly decomposed that they do not, as a rule, appear in the gas passing out of the producer. The carbonaceous residue (coke) is subsequently completely gasified in the lower layers of the

incandescent fuel bed, by interaction with the ascending air-steam blast, yielding a mixture of CO_2, CO, H, and N, together with further small porportion of NH_3 and CH_4. The proportion of CO_2, CO, and H leaving the incandescent coke bed depend upon the steam saturation temperature of the blast, which also largely determines the temperature gradient throughout the fire. In order to fully understand the chemistry of the process, it is necessary to separately consider the interaction between incandescent carbon and air and steam respectively. In a solid bottom producer operated with a *dry*-air blast, the initial action of the oxygen upon the incandescent carbon is rapidly succeeded by the reversible reaction $2CO \rightleftharpoons C+CO_2$ in which the state of equilibrium is a function of both temperature and the partial pressures of the CO and CO_2. It can be demonstrated that the time required for the establishment of this equilibrium, at the temperatures which prevail in the fuel bed, is far shorter than that occupied by the gaseous mixture in traversing the fuel. According to Rhead and Wheeler's experiments (Chem. Soc. Trans. 1910, 2178), the equilibrium in the system $2CO \rightleftharpoons C+CO_2$ at atmospheric pressure varies with temperature as follows :—

	Per cent.	
Temp.	CO_2	CO
850°	6·23	93·77
950°	1·32	98·68
1050°	0·37	99·63
1200°	0·06	99·94

results which are in agreement with the thermodynamical equation

$$\frac{19{,}500}{T_{abs.}} + \log_e \frac{C_{2CO}}{C_{CO_2}} = 20{\cdot}4.$$

As the change from 2CO to CO_2 involves a diminution in volume, it can be predicted on thermodynamical grounds that a lowering of the partial pressures of the CO_2 and CO, consequent on dilution with N in the producer gases, will affect the equilibrium in the same direction as an increase in temperature, *i.e.* it will tend to increase the ratio CO/CO_2 at any given temperature. The temperatures in the active zones of the fuel bed of an air-blown producer gasifying coal or coke may vary between 1250° and upwards of 1400°, and with good coke it is easily possible to generate a gas containing 0·5 CO_2, 33·0 CO, 1·5 H, and 65·0 p.c. N. But since the combustion of carbon to CO liberates approximately 30 p.c. of its total heat of combustion, not only would the thermal efficiency of the gasification in an air-blown producer, reckoned on the cold gas, be low, but the high temperatures in the fuel bed would cause serious clinkering troubles in cases where the fuel leaves a fusible ash. In the Thwaite cupola producer (30 feet high and 6 feet internal diameter), where a dry-air blast, forced in through a series of twyers near the bottom, is employed, it is usual to add a certain proportion of limestone to the fuel charge in order to form a liquid slag with the ashes, which is tapped at intervals through a slag-notch. Working on a Lancashire slack coal, this producer yields a gas containing 2·0 CO_2, 29·0 CO, 5·35 H, 2·05 CH_4, 61·6 N, of cal. value 130·8 *net*, and 138·7 *gross*, B.Th.Us. per cub. ft. at 0° and 760 mm.

Steam reacts with carbon in two ways, namely, (1) $C+2H_2O=CO_2+2H_2$, and

(2) $C+H_2O=CO+H_2$,

and both reactions are strongly endothermic. At 500°–600° (1) predominates; as the temperature rises (2) gradually asserts itself, until at 1000° and upwards it occurs exclusively. The function of the steam in a gas producer is, therefore, to absorb some of the heat liberated during the partial 'air combustion' of the carbon to CO by doing chemical work, thereby raising the potential energy of the resulting gas at the expense of some of its sensible heat. Incidentally, also, clinkering troubles with a fusible ash are greatly diminished by the admixture of steam in the blast. Where a large proportion of steam is used, the composition of the resulting gas is appreciably affected by the reversible system $CO+H_2O \rightleftharpoons CO_2+H_2$, of which the equilibrium constant, $\frac{CO \times H_2O}{CO_2 \times H_2} = K$, increases with temperature (according to O. Hahn, K=0·81 at 786°, 1·54 at 986°, and 2·10 at 1205°). The operation of this reversible reaction must also be considered when a producer gas passes through the hot regenerators of an open-hearth furnace.

The influence of varying blast-steam saturation temperatures upon the composition and yield of the gas from a Lancashire bituminous coal containing C=78·0, H=5·4, S=1·0, N=1·4, O=10·0, ash=4·2 p.c., and yielding 36 p.c. 'volatiles' at 900°, is shown in the tabulated results (p. 619) of a series of gas-producer trials (each extending over a continuous period of 100–130 hours) carried out by Bone and Wheeler in 1906–7 (Jour. Iron and Steel Inst. 1907, i. 126; 1908, ii. 206).

In these trials it was also proved (1) that on gasifying an ordinary bituminous coal by means of a mixed air-steam blast, about 92·5 p.c. of the carbon in the fuel is converted into permanent gas (CO_2, CO, and CH_4), another 6·3 p.c. appears as tar, and the remaining 1·2 p.c. is lost in the ashes. These proportions are independent of the blast-steam saturation temperature. (2) That with blast-steam saturation temperatures up to and including 55°, the whole of the steam in the blast is decomposed in passing through the fuel bed; as the saturation temperature is raised above this limit, the proportion of the steam decomposed progressively diminishes, although the absolute quantity (per lb. of fuel) increases. (3) That increasing the effective depth of fuel bed beyond 3 feet 6 inches has no influence upon either the composition of the gas or the practicable rate of gasification. (4) That the thermal efficiency of the gasification reaches a maximum at blast-steam saturation temperatures between 50° and 60°, and that the best quality of gas for furnace purposes is produced with a saturation temperature of 50°.

In gas generated for furnace purposes it is important that the CO content should be as high as possible, and that the H content should not exceed about 12–14 p.c.; moreover, for a regenerative furnace supply the gas leaving the producer should be in a hygroscopic condition such that the proportions of CO_2, CO, H, and H_2O shall substantially conform to the equili-

Average depth of incandescent fuel	3 feet 6 inches					7 feet				
Average rate of gasification (day-shift) per hour per producer	22·5 cwts.					11·5 cwts.				
Steam saturation temperature of blast	45°	50°	55°	60°	70°	60°	65°	70°	75°	80°
Percentage composition of the gas: Carbon dioxide	2·35	2·50	4·40	5·10	9·25	5·25	6·95	9·15	11·65	13·25
Carbon monoxide	31·60	30·60	28·10	27·30	20·85	27·30	25·40	21·70	18·35	16·05
Hydrogen	11·60	12·35	15·45	15·50	19·75	16·60	18·30	19·65	21·80	22·65
Methane	3·05	3·00	3·00	3·05	3·45	3·35	3·40	3·40	3·35	3·50
Nitrogen	51·40	51·55	49·05	49·05	46·70	47·50	45·90	46·10	44·85	44·55
Total combustibles	46·2	45·95	46·60	45·85	44·05	47·25	47·10	44·75	43·50	42·20
Calorific value of the gas, B.Th.U. per cubic foot at 0° and 760 mm.: Gross	180·0	178·5	180·8	178·7	175·5	185·6	185·4	177·5	172·0	169·5
Net	170·5	168·7	169·1	166·9	161·0	173·0	172·0	163·3	157·3	154·3
Yield of gas, cubic feet, at 0° and 760 mm. per ton coal	133,700	132,500	132,700	135,000	—	138,250	134,400	141,450	145,800	147,500
Steam added to blast, lbs. per lb. coal	0·2	0·21	0·32	0·45	—	0·45	0·55	0·80	1·10	1·55
Percentage steam decomposed	all	all	all	76·0	—	87·0	80·0	61·0	52·0	40·0

brium *ratio* corresponding to the highest temperature of the regenerator (say 1200°), namely, $\frac{CO \times OH_2}{CO_2 \times H_2} = 2{\cdot}0$. This latter requirement is fulfilled by a gas containing 2·5 CO_2, 30·6 CO, 12·35 H (such as may be generated with blast-steam saturation temperature of 50°), and leaving the producer in a hygroscopic condition corresponding to saturation at 20°. Such a gas will leave the producer heavily charged with tarry vapours, and at a temperature of 500°–600°; it usually passes on to the furnace through large fire-brick lined mains, without being cleaned or cooled, accumulations of tar, soot, &c. in the mains being burnt out in a current of air at the end of each week's run (*vide* also W. A. Bone, Producer Gas, with special reference to Steel Works Requirements, Journ. W. of Scotland Iron and Steel Institute, 1911).

In gas generated for power purposes, the actual composition is not so important, provided that the total content of combustible constituents is high, and in such cases the gas may be generated under conditions permitting of the recovery of a large proportion of the N in the fuel as NH_3. A gas supply for internal-combustion engines must be both thoroughly cleaned and cooled down to atmospheric temperature before delivery to the engine.

The main points to be considered in relation to gas-producer design are: (1) the easy and accurate control of the blast-steam saturation temperature; (2) a suitable form of grate or twyer which should permit of a rapid rate of gasification, together with uniform distribution of the blast through the fuel bed; (3) the contour of the furnace body; and (4) the arrangements for charging the producer and removal of the ashes. One of the earliest forms of gas producers (Ebelmen, 1840) was of the cupola type, in which charcoal or coke was gasified, with a positive blast introduced through twyers, limestone being added to the charge (if necessary) to flux the ash. In 1845 Ekman, a Swedish ironmaster, designed a furnace and producer combined, for which the fuel was charcoal. The producer itself consisted of a cylindrical fire-brick chamber, enclosed in an iron casing, a space being left between the brickwork and the casing through which the air supply was admitted and preheated on its way to the fire. In 1861 the Brothers Siemens patented their well-known producer for use in connection with their new regenerative furnace. This producer consisted of a fire-brick chamber, rectangular in section, the front of which was inclined at an angle of 45°–60°, provided with a grate at the bottom, through which a current of air was induced. Below the grate was a trough of water, which, on evaporation, by heat radiated from the grate, added a certain proportion of steam to the induced air supply. Subsequently the front of the producer was closed by an iron door, and the air supply forced in under the grate by steam injection. This producer was the first to successfully gasify a bituminous coal; it was capable of generating a fairly good quality of gas, but its rate of gasification was low. In 1876 Messrs. Brooke and Wilson patented a producer consisting of a cylindrical chamber having a solid hearth, but no fire bars. The mixed air-steam blast was obtained by steam injection, and was introduced into the fuel bed by means of a box-shaped casting which traversed the middle of the hearth. In 1882 Mr. Wilson patented a form of generator on which ash and clinker were automatically removed by means of two worm screws revolving in a water seal. Water-sealed producers have now almost entirely superseded the older solid or bar-bottom types.

The Duff producer (Fig. 4) may be cited as modern producer of simple design; it consists of a cylindrical chamber, A, 7–10 feet internal diameter, with a 9-inch fire-brick lining within an outer steel shell. At the bottom of the lining is a circular angle-iron casting, which dips

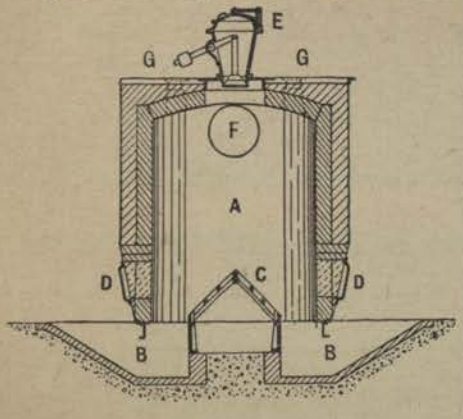


FIG. 4.

into the water seal in the trough BB. The 'Duff' grate, or blast grid, C, is a /\-shaped structure, with transverse grids extending as a ridge across the producer immediately above the water seal; the air-steam blast enters the space beneath the grate, and the grid ensures its uniform distribution over a considerable area of the fuel bed. The latter (which, as a rule, extends to a height of about 3 feet above the apex of the grate) is supported upon a bed of ashes, which extends downwards from the grate level into the water trough. In the lower part of the shell of the producer, and on a level with the grate, are inserted cleaning doors DD. The fuel is charged intermittently into the furnace through the belled hopper E, and the gas outlet is at F; the dotted lines at GG indicate poking holes. Ashes are withdrawn from the water trough at regular intervals in quantity corresponding to the rate of accumulation in the furnace. A producer of 10 feet internal diameter will gasify 10 cwts. of coal per hour, or about 15 lbs. per sq. ft. of fire area.

In Fig. 5 is shown the latest form of the Mond producer, which, although designed with special reference to ammonia-recovery practice, is eminently adapted to all working conditions. The chief features about this producer are (1) the annulus A between the inner fire-brick lining and outer steel shell through which the incoming preheated air-steam blast passes before reaching the grate; (2) the hanging bar grate B, which takes the shape of an inverted truncated cone, with spaces between the bars for the admission of the blast, an arrangement which ensures an adequate grate area and a very uniform and effective distribution of the blast in the fuel bed; and (3) the large bell C at the top of the producer below the charging hopper D, which is supposed to expedite the preliminary distillation of the raw fuel. The Mond producer is usually worked with a very deep fuel bed, as indicated in the diagram, but if the bell C be dispensed with, a much shallower fuel bed may be used with advantage. In Fig. 6 is shown the 'Alma' producer, which, with an improved form of hanging bar grate, is specially adapted

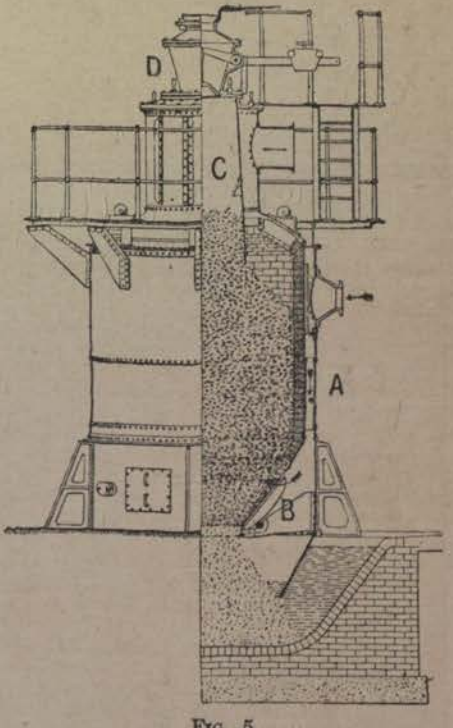


FIG. 5.

for rapid gasification with a shallow fuel bed. In a producer of this type, 10 feet internal diameter, from 20 to 25 cwts. of coal (equal to 30–35 lbs. per sq. ft. of fire area) may be gasified per hour.

Within recent years attention has been drawn to the automatic and continuous feeding of the fuel into producers so as to ensure a more even distribution over the fire bed, and more uniform working conditions. The 'George' feed of the Morgan producer (Fig. 7) satisfactorily effects this purpose. The essential feature of this device is an inclined and slowly rotating water-cooled feeding spout A, fixed immediately under the charging hopper B, the fuel being continuously forced from B into A by the slowly

revolving circular disc, C, working up against the fixed bracket D. The producer itself is water

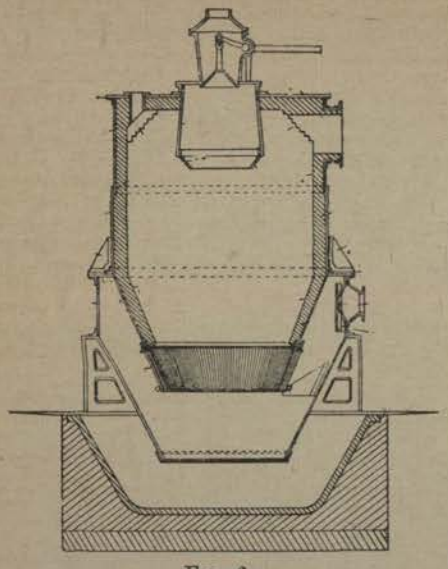


FIG. 6.

sealed, and circular in section, but tapering from the middle downwards. The blast is introduced through the central dome E, and the gas outlet is at F. The producer may be worked with a shallow fuel bed (3 feet thick), and with a fire

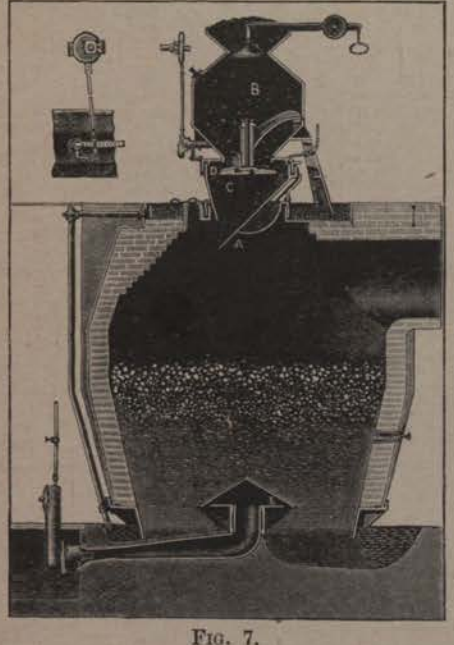


FIG. 7.

of 10 feet diameter will gasify about 10 cwts. of fuel per hour.

The Kerperley producer (Fig. 8) embodies the latest device for the automatic and continuous removal of ashes, consisting of a revolving conical grate, A, fixed eccentrically upon the foundation, and provided with a flattened top. The cone comprises a number of plates through which the steam-air blast reaches the fire. The

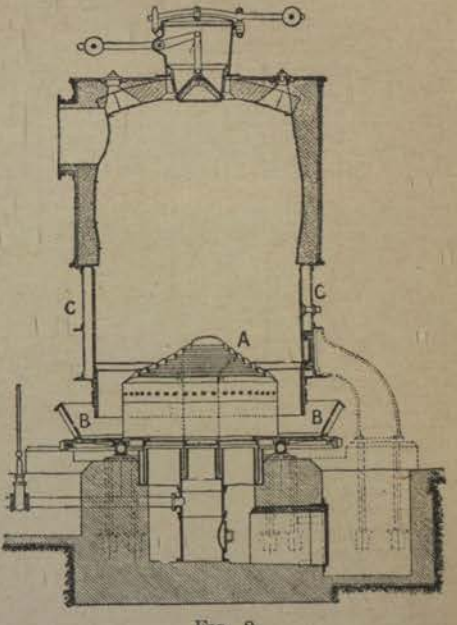


FIG. 8.

grate is fixed in one piece with the shallow iron water trough BB, which is continuously rotated at the slow rate of one revolution every 2½–3 hours. The lower part of the producer surrounding the zone of active chemical action is water-jacketed CC, in order that no incipient clinkers can adhere to the cold side plate. The slowly revolving eccentric grate disintegrates clinkers before they attain large dimensions, and, pushing the ashes outwards into the water trough, causes them to be automatically discharged by their coming up against a fixed scraper. The Morgan producer also is now fitted with a mechanical revolving grate (Fig. 9), which,

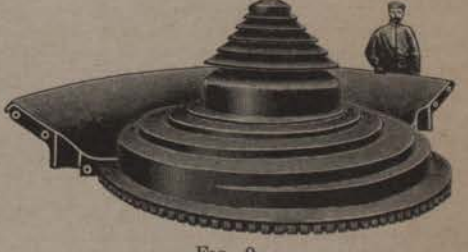


FIG. 9.

besides effecting automatic discharge of ashes, considerably increases the gasifying capacity of the producer.

All large gas producers are blown on the pressure system either by means of steam

injection or preferably by a suitable fan or blower, steam or electrically driven. The pressure required is only 3–6 inches water gauge, according to the thickness of the fire. In the case of a blower-produced blast, the requisite steam is introduced through a lateral opening into the air duct a few feet before it enters the producer; perfect control and adjustment of the blast-steam saturation temperature is of great importance in relation to uniform working.

For the cleaning and cooling of producer gas for gas engines, various arrangements of plant are employed, comprising (1) a dust-catching chamber; (2) atmospheric condenser, usually of annular type; (3) water-sprayed coke or 'hurdle' scrubbers; (4) water-sprayed fans; and, finally (5) sawdust scrubbers or other equivalent devices for removal of tar fog.

For small (up to 100 h.p.) power installations, producers in which the blast is induced by the suction of the engine cylinder ('suction producers') are now largely employed with anthracite or coke as fuel. The first successful attempt to operate a producer by suction in conjunction with a gas engine was made by Léon Bénier, in 1896, who employed a suction pump, placed side by side with the engine cylinder and driven by means of a connection with the fly-wheel axle. Soon afterwards the suction of the engine itself, on the out-stroke of the piston, was substituted for the Bénier suction pump, thus cheapening construction, and at the same time reducing frictional losses. By 1901 'suction' power plants were established on the market, and their use has since steadily extended. Such a plant (as illustrated in Fig. 10) consists of the

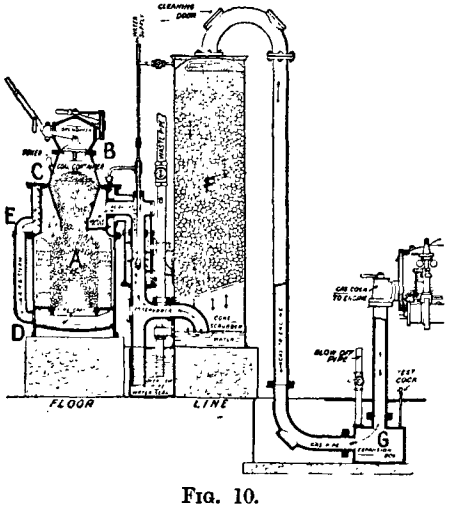


FIG. 10.

following essential parts: (1) A fire-brick-lined *generator*, A, of cylindrical section, in which the fuel is gasified by means of an air-steam induced draught; the fuel is introduced through an *air-tight feeding hopper*, B, which drops it into a *storage and distillation bell*, C, situated within the generator. The fire rests upon a horizontal grate under which is a shallow chamber, D, with a solid bottom, and a lateral opening communicating with the air and steam supplies. (2) A *vapouriser*, E, which may be either within or without the upper part of the shell of the generator, in which a regulated water supply is vapourised, usually at the expense of some of the sensible heat of the hot gas leaving the generator, or sometimes by the heat of the fire. (3) A water-sprayed *coke scrubber*, F, for cooling and washing the gas; and (4) an *expansion box*, G, which serves the double purpose of a gas reservoir for the engine, and, on the suction stroke, of minimising the jerkiness of the suck. The generator is started up by kindling a wood fire on the grate with a layer of coke or anthracite above. The fire is blown up by means of a hand fan, which is a necessary auxiliary to the apparatus. During the starting-up period, the products of combustion are sent into the atmosphere through a vent pipe, but as soon as a rich enough gas is generated (about 20–30 minutes from the start), the engine is started and the fan shut off. A typical 'suction gas,' generated from gas coke with air saturated with steam at 51·7°, contains CO_2=5·10, CO=25·45, H=13·10, CH_4=0·28, and N=55·32 p.c., its *net* calorific value being 127 B.Th.Us. per cub. ft. at 0° and 760 mm. The thermal efficiency of the gasification, allowing for the power required to draw the gases through the system, and based on the net calorific values of coke and gas respectively, is about 78·5 p.c. The fuel consumption on a suction plant is about 1 lb. or even slightly less, per b.h.p. developed, the water consumption for scrubbing the gas being about 1·2 gallons per b.h.p.

Ammonia-recovery systems. The solution of the problem of the gasification of coal under conditions which permit of the recovery of a large proportion of its nitrogen as ammonia, was due to the late Dr. Ludwig Mond. The best practical results are obtained by working the producer with a blast-steam saturation temperature of 85°, the mixture of air and steam being preheated to about 250° before it enters the fuel bed. There is carried into the producer by the blast about 2 lbs. of steam for every 1 lb. of coal gasified; one-third only of this steam is decomposed, by interaction with carbon, in passing through the fuel bed, the remaining two-thirds passing with the hot gases out of the producer. The outstanding features of the process are (1) that, owing to the cooling influence of the large proportion of steam in the blast upon the fuel bed, the low temperature interaction $C+2H_2O=CO_2+H_2$ predominates over the high temperature 'water-gas' reaction, $C+H_2O=CO+H_2$, so that the resulting gas (*e.g.* 17·0 CO_2, 11·0 CO, 24·0 H, 3·0 CH_4, and 45·0 N) has a high hydrogen and low carbon monoxide content as compared with ordinary producer gas; and (2) that for economical working it is necessary that the large proportion of steam leaving the producer shall be conserved to the system by some efficient recuperative arrangement. From a coal containing between 1·2 and 1·6 p.c. N it is possible to obtain up to 90 lbs. per ton of ammonium sulphate, together with about 150,000 cub. ft. of gas (at 0° and 760 mm.) of calorific value about 150 gross and 135 net, B.Th.Us. per cub. ft. at 0° and 760 mm. According to the Mond system of ammonia recovery and steam recuperation, as originally designed, the gas leaves the producer heavily

charged with steam and tarry vapours at a temperature of 500°–600°. It then traverses the central tubes of a series of three annular 'superheaters,' indicated by B in the diagram (Fig. 11), each about 20 feet long. The incoming steam-air blast passes through the annulus between the central and outer tubes in the reverse direction. The temperature of the gas is thus reduced to about 250°, whilst that of the blast is raised to about 200° (further 'superheating' of the blast occurs as it subsequently traverses the annulus between the fire-brick lining and the outer steel casing of the producer itself). The partly cooled gas next passes through a long rectangular and water-sealed chamber (the 'mechanical washer'), C, where it encounters a water spray thrown up by a series of revolving dashers, by which means dust, soot, and a large amount of heavy tar are removed, and the gas itself further cooled to about 100°. It next passes up the lead-lined scrubbing tower D, packed with perforated bricks or tiles, down which an acid liquor containing 36–38 p.c. of ammonium sulphate *plus* 2·5 p.c. of sulphuric acid is sprayed, the volume of liquor being so adjusted in relation to the upward flow of gas that the latter leaves the tower at a temperature of 80° and free from ammonia. The tarry liquor from the tower is passed through a separator whereby partial separation of liquor and tar is effected; to the main bulk of the clear liquor is added a regulated quantity of sulphuric acid, after which it is again pumped up to the top of the acid tower D. A portion of the clear liquor is, however, removed from the circuit, and, after treatment with heavy oils (if necessary) to remove tar, is evaporated to crystallising-point in a conical lead-lined vessel furnished with steam coils. After separation of ammonium sulphate, the mother liquor is pumped back into the main-liquor circuit. The ammonia and tar-free gas, on leaving the acid tower at 80°, is passed up the 'gas cooling tower' G, where it encounters a downward spray of cold water, so regulated that whilst the gas is cooled down to 40°–50°, and rendered substantially free from tar, the water is heated up to 75°–78°. The gas passes onwards to the place of consumption, but if intended for gas engines it should be further cooled down to within a few degrees of the atmospheric temperature, and be also passed through a sawdust scrubber to remove the last traces of tar.

The hot water from the 'gas-cooling tower' is passed through a tar separator, after which it is pumped up to the top of the 'air-saturating tower' K down which it is sprayed. The air blast for the producer is forced up this tower by means of a blower; in this way the blast is heated up to and saturated with steam at 75° at the expense of the hot water. A further quantity of live steam is added to the air blast as it passes forward to the superheaters in order to raise its steam-saturation temperature to 85°.

The chief drawback to the original Mond system was the large capital outlay involved, which rendered ammonia recovery unprofitable unless the coal gasified exceeded 180–200 tons per week. Moreover, the gas, being rich in hydrogen and poor in carbon monoxide, is not well suited for open-hearth steel or glass-melting regenerative furnaces.

Successful efforts have been made to simplify the mode of ammonia recovery by the substitution of rectangular horizontal washers, constructed of steel or iron work and rendered resistant to the acid liquor by special

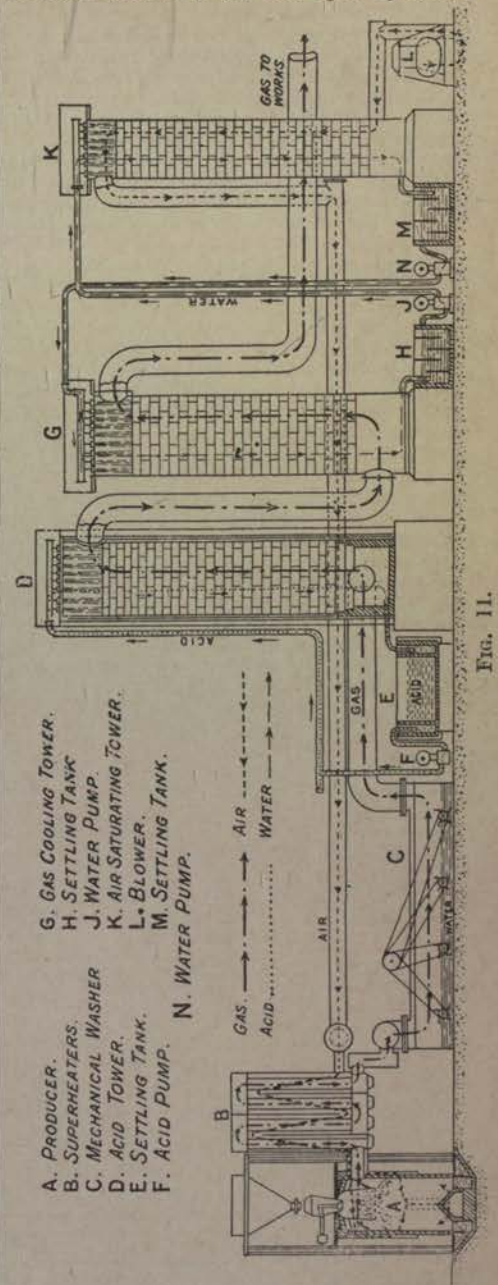


FIG. 11.

treatment, for the expensive lead-lined vertical acid tower, and by making the sulphate liquor play the double *rôle* of an absorbent for the ammonia in the gas and an agent for the transfer of undecomposed steam back to the

producer blast. As an example of this type of plant, the Crossley and Rigby system may be described with reference to Fig. 12. The generator A is central blown with a special rotary conical grate (1 revolution in 4 hours), which gives an even distribution of blast through the deep fuel bed and minimises clinker formation. The blast enters the fuel bed preheated to 280° and with a steam-saturation temperature of 85°. The gas, on leaving the producer, passes through the tubular 'superheater' B, so designed as to give a maximum of heating surface combined with facility of cleaning. The latter operation may be effected whilst the plant is running by means of a corkscrew cleaner inserted through holes provided at the top. The function of the superheater is to effect a transfer of part of the sensible heat of the outgoing hot gas to the incoming steam-air blast. The partly cooled gas next passes onwards to the 'washer condenser' C, consisting of five compartments, in the first two of which it meets with a water spray whereby it is freed from dust and heavy tarry vapours; the steam generated is subsequently recovered. In the remaining three compartments the gas is washed with a spray of sulphate liquor containing 0·5 p.c. of free acid, which is circulated by gravity flow in a direction contrary to that of the gas. The absorption of ammonia is complete, whilst at the same time the gas is satisfactorily cooled and most of the undecomposed steam leaving the producer is condensed. After leaving the washer condenser, the gas is slowly filtered through the dry coke scrubber D whereby all trace of sulphate liquor spray is removed. The hot liquor from the washer condenser passes by gravity flow into the well E whence it is pumped into the air-saturating chamber F where it flows and is sprayed by paddles in a counter direction to the cold-air blast created by the blower G. The liquor is thereby cooled and flows by gravity back to the washer condenser C, whilst the air blast is warmed and leaves the chamber (*viâ* the coke scrubber H) saturated with steam at 75°. A constant proportion of sulphate liquor is withdrawn from circulation and delivered into the closed evaporator K, where it is concentrated to crystallising-point. A portion of the concentrate is run off at frequent intervals into the crystallising trough L, where, after cooling and draining, the sulphate is dried and the mother liquor returned by gravity flow to the washer condenser C. The steam from the evaporator is conveyed by an overhead pipe to the base of the coke scrubber H, where it enters the air blast already saturated with steam at 75°. The steam-air blast then passes forward, *viâ* the coke scrubber H and the superheater B, to the producer. Owing to a special treatment of the iron and steel used in the construction of the plant, all leadwork is eliminated, except in the acid storage tank and the sulphate concentrating and crystallising apparatus. In consequence of the greatly reduced capital cost, as compared with the original Mond system, it is now possible to carry out ammonia recovery when gasifying only 100 tons per week. From a producer coal of average quality, containing 1·20–1·25 p.c. N, and up to 10 p.c. ash, it is possible to recover 90–100 lbs. of sulphate per ton, together with 140,000 cub. ft. of gas (at N.T.P.)

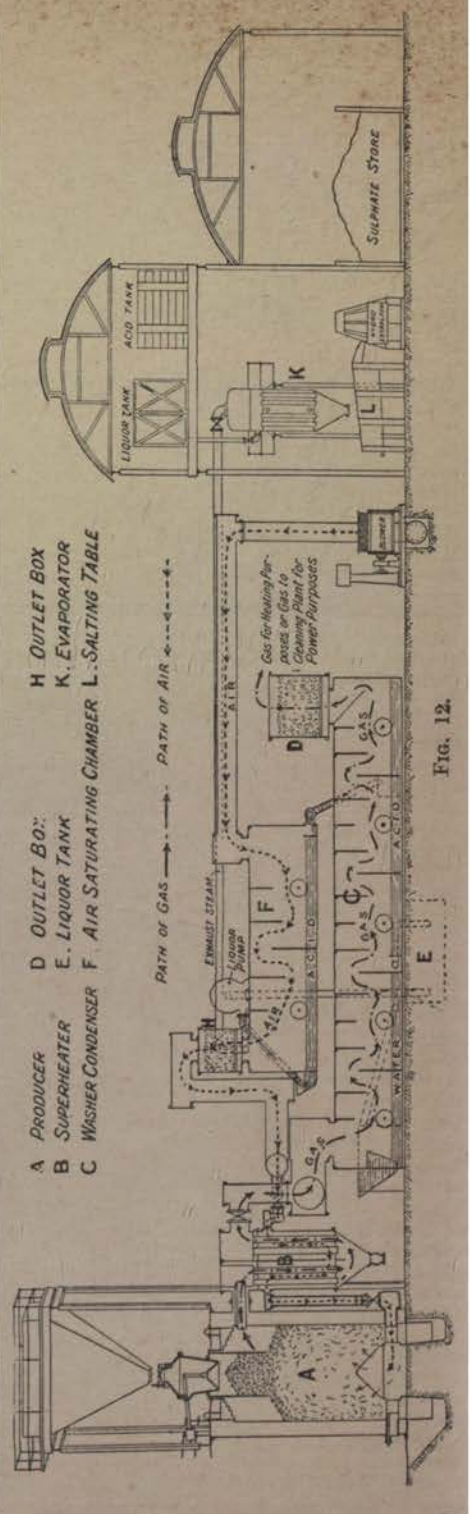


FIG. 12.

containing 16·5–17·0 CO_2, 10·5–11·0 CO, 26·5–27·0 H_2, and 2·6–2·8 CH_4.

Blast-furnace gas. Within recent years the problem of better utilising the waste gases from iron blast-furnaces as a source of power has assumed great industrial importance. A furnace smelting an average grade of ore, with coke as fuel, will yield per ton of iron produced about 168,000 cub. feet of gas at 15° and 760 mm. containing approximately 12·0 CO_2, 30·0 CO (this may include from 0·5–1·0 H) and 58·0 N, of calorific value approximately 95–100 B.Th.Us. per cub. ft. For a furnace with an output of 1000 tons of pig iron per week, the production of gas will average 1 million cub. ft. per hour, the potential energy of which is about 45 p.c. that of the coke charged into the furnace. Until the year 1837, when the French ironmaster Dufaur drew attention to the matter, this immense amount of energy was entirely wasted. The classical investigations of Bunsen at Verkerhagen in 1838, and of Bunsen and Playfair at Alfreton in Derbyshire in 1844–5 (Brit. Assoc. Reports, 1845; reprinted, 1903, by the Iron and Steel Inst.), finally led to the utilisation of the gases for (1) heating the blast for the furnace, and (2) boiler firing. Special 'hot-blast' stoves, on the regenerative principle, were designed to effect the first purpose by E. A. Cowper and by Thomas Whitwell in 1865, whilst for steam raising the gas was burnt in a fire-brick-lined combustion chamber attached to a Lancashire boiler. In this way about half of the gas was utilised for heating the blast, and a further 40 p.c. would suffice to raise steam for driving the blowing engines, the furnace hoists, and other mechanical appliances in connection with the plant, leaving a surplus of about 10 p.c. not utilised. But the combined efficiency of boiler *plus* steam engine was always very low; thus in 1902 it was estimated by a Cleveland engineer that with the best type of water-tube boiler only about 54 p.c. of the heat developed by the combustion of the gas is actually transmitted to the water, and that the combined efficiency of boiler and blowing engine was somewhat less than 7 p.c. All this has been changed by the rapid development of the large gas engine during 1895–1905, which has increased the efficiency of power production from blast furnace gas something between three- and fourfold as compared with the old steam plants. Gas engines developing 1000–2000 b.h.p. per unit have now been installed in most of the German and many British and American ironworks, realising in actual practice a thermal efficiency of conversion 'gas—b.h.p.' of 25 p.c., and of 'gas—e.h.p.' of 20–22 p.c. As an illustration of what this improved practice implies in regard to surplus power production, the following figures may be quoted for a plant of four furnaces smelting 3200 tons of iron per week from calcined Cleveland ironstone; the hourly production of gas is 3,200,000 cub. ft., of which approximately 1,600,000 are required for heating the blast, and a further 400,000 cub. ft. for operating an electrically driven blowing engine; the balance of 1,200,000 cub. ft. will, when used in a gas engine coupled with a dynamo, give 9000 e.h.p. at the switchboard continuously day and night. Some 40 p.c. of this would suffice to provide all the power required in connection with the steel plant and electrically driven rolling mill for converting the iron into steel and rolling it into rails or girders; the remaining 60 p.c. would represent 'surplus' power available for other purposes.

The gas, as it leaves the furnace at a temperature of 300° or thereabouts, is heavily charged with dust, which must be reduced by washing to infinitesimal proportions before it is fit for delivery to the engines. The cleaning of the gas is usually accomplished in two or three stages, namely: (1) 'dry cleaning' (by means of any ordinary type of dust catcher), which may reduce the dust down to between 2 and 8 grams per cub. metre; (2) preliminary water washing (*e.g.* in the Bian washer, consisting of a cylindrical steel chamber along the axis of which there slowly revolves a horizontal shaft carrying a series of circular discs of thick wirework with a coarse mesh, the lower half of which is submerged in water; the dusty gas is partly cleaned by passing through the films of water between the wire meshes); this may reduce the dust down to 0·5 gram per cub. metre; and (3) a final cleaning in some form of centrifugal apparatus in which the gas is violently churned up with a fine spray or stream of water (*e.g.* the Theisen washer). Most frequently the cleaning is carried out by the combination of processes (1) and (3) only. In any case, the dust in the gas should be reduced down to about 0·01 gram per cub. metre, and the temperature to 18°–20°, before delivery to the engine. The power expended in cleaning the gas to this degree amounts to between 5 and 6 p.c. of that generated by its explosion in the engine cylinder.

Water gas. The need of a cheap gaseous fuel of high calorific intensity for certain industrial purposes (*e.g.* steel welding) has led to the utilisation of the well-known endothermic interaction of steam and incandescent carbon at high temperatures. For such a process to be continuous, heat would have to be transmitted from an external source through the walls of the reaction chamber or retort, which would necessarily be constructed of refractory material of low conductivity. As such procedure would certainly be very uneconomical, all idea of it has been abandoned in favour of an intermittent process, in which a bed of fuel (usually coke) is alternately blown with (1) air, until the mass attains a sufficiently high temperature, and (2) with steam, so long as the high temperature interaction $C+H_2O \rightleftharpoons CO+H_2$ can proceed without undue occurrence of the low temperature interaction $C+2H_2O \rightleftharpoons CO_2+2H_2$.

The use of water gas was first introduced in the United States about the year 1875, as the result of the pioneering efforts of J. S. C. Lowe, but it was not until 1888 that the British Water Gas Syndicate installed the first plant in Great Britain at the Leeds Forge. This plant embodied the now obsolete idea of, during the 'air blow,' manufacturing a low grade 'producer gas' (a mixture of CO_2, CO, and N, in which CO was the predominating carbon constituent), for furnace purposes by blowing a thick fuel bed with an air blast at moderate pressure. This operation was alternated with the usual 'steam

blow' for the production of 'water gas.' The 'air blow' occupied 10 minutes, and the 'steam-blow' only 4 minutes, and each ton of gas coke yielded about 34,000 cub. ft. of 'water gas,' and about 140,000 cub. ft. of 'producer gas,' some 25 p.c. only of the carbon in the fuel appearing in the 'water gas.'

Some ten years later the process was much improved by Dellwik and Fleischer, who proposed, during the air blow, to heat up a comparatively thin bed of fuel as rapidly as possible by means of a blast supplied in such quantity as to burn the carbon as completely as possible to the dioxide. In the Dellwik-Fleischer system (Figs. 13 and 14), the generator is of cylindrical section with a fire-brick lining

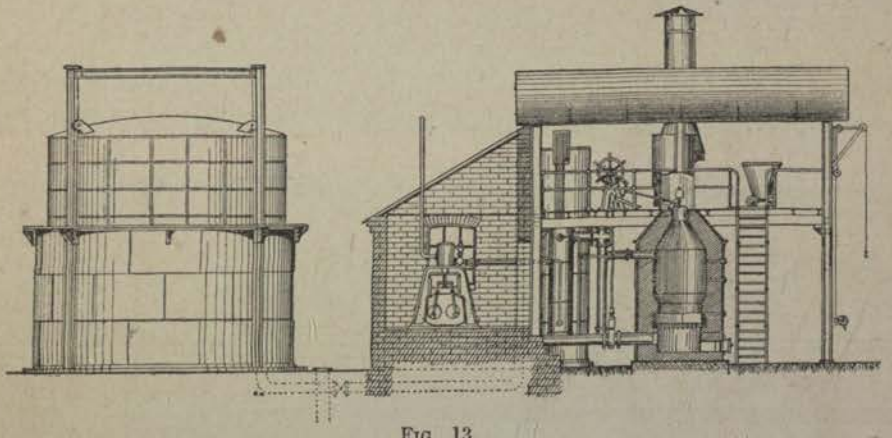


FIG. 13.

encased in a steel shell. The fuel bed rests on a flat bar grate on a level with which are clinkering bars, and below which are doors for the removal of ashes. The air blast always enters the fuel bed from below through a valve, and the products of the 'air blow' leave the generator by the central stack valve, through which also the fuel is charged from a small hopper waggon. During the 'steam blows' superheated steam

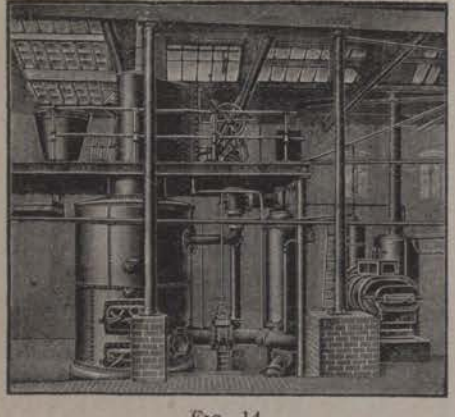


FIG. 14.

from a boiler working at a pressure of 150–160 lbs. per sq. in. is blown through the incandescent fuel bed in either an upward or a downward direction, the direction being reversed in each successive blow. Accordingly, there is one 'water-gas' outlet at the top of the generator, and another below the grate, each provided with a valve leading to the annular 'superheater,' which serves to effect a heat exchange between the outgoing hot gas and the incoming steam blast, thus superheating the latter. At the bottom of the 'superheater' is a water seal through which the gas passes onwards to a coke scrubber, where it is cooled and cleaned from dust by means of a water spray; from thence the cold gas passes into a holder. The various valves of the generator are operated by an interlocking gear which makes it impossible for the operator to make a mistake or get an explosive mixture in any part of the plant. A set of water gauges and a test flame on the operating platform indicate the working conditions in the generator at any moment and also the quality of the gas during the 'steam blow.' Towards the end of the 'steam blow,' when the temperature of the fuel has fallen below the point at which the low temperature interaction $C+2H_2O \rightleftharpoons CO_2+2H_2$ comes seriously into play, the steam and gas valves are shut off, the stack and air valves being simultaneously opened, for the commencement of the 'air blow.' Each 'air blow' lasts about 1 minute, and the subsequent 'steam blow' about 4 minutes. With an average quality of gas coke the plant will produce about 32 cub. ft. at 0° and 760 mm. of water gas per lb. of carbon charged into the generator, which means that as nearly as possible 50 p.c. of the carbon is converted into water gas. The average composition of the gas is 4·0 CO_2, 43·0 CO, 49·0 H, 0·5 CH_4, and 3·5 p.c. N, and its calorific value about 320 gross and 290 net B.Th.Us. per cub. ft. at 0° and 760 mm. The *ratio* of the net calorific value of the gas to that of the coke charged into the generator is about 0·60.

Another system of water-gas making is that embodied in the Kramers and Aarts patents (the 'K and A' system), according to which two generators, A and B (Figs. 15, 16, and 17), connected through a double 'regenerator,' C, are operated in parallel during the 'air blow'

and in series during the 'steam blow,' somewhat as follows :—

During the 'air blow' the fires (5-6 feet in thickness) in both regenerators are simultaneously blown in parallel by a powerful blast, which is introduced from below each fire. The hot

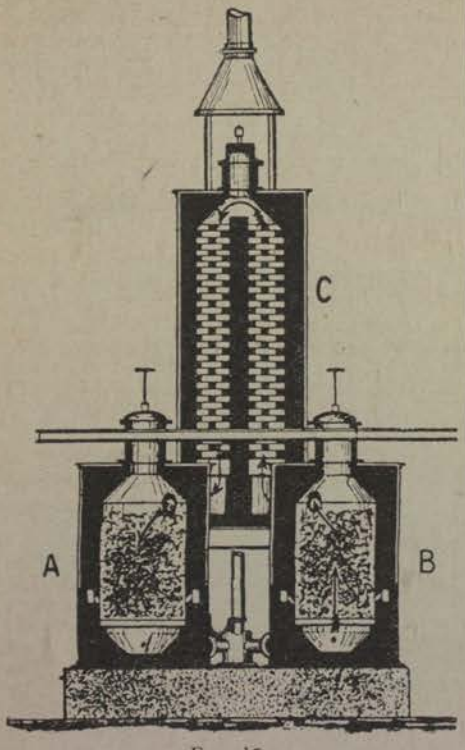


FIG. 15.

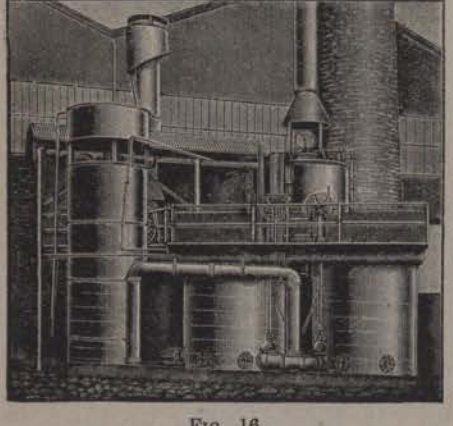


FIG. 16.

products (CO_2, CO, and N), on leaving the top of the generators, pass upwards through the 'double regenerator,' a cylindrical structure filled with fire-brick chequer work and divided vertically into two chambers or compartments by a central fire-brick wall. As the hot products enter in parallel streams at the base of one or other of the two chambers, they meet a secondary air supply sufficient to burn completely all the CO

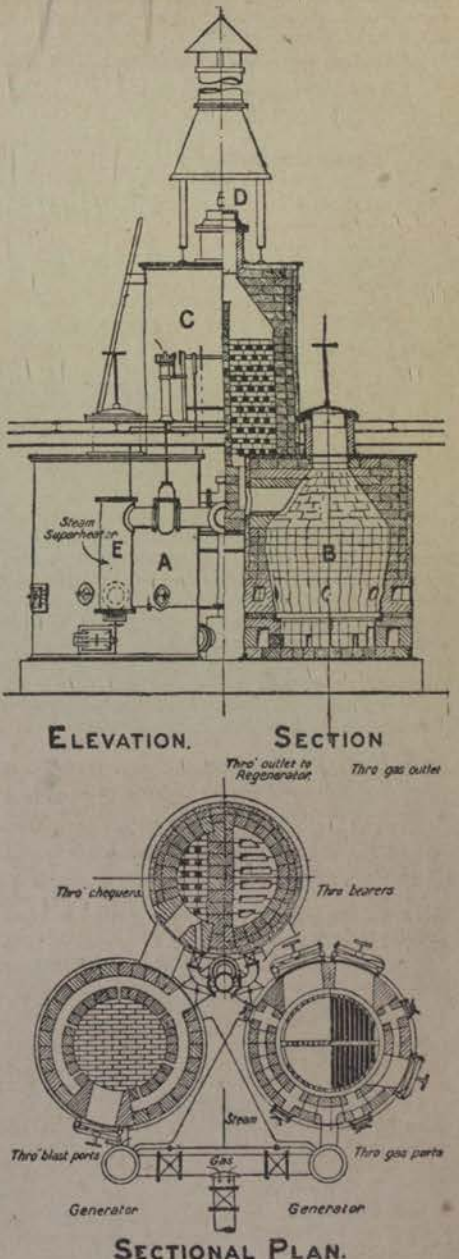


FIG. 17.

which they may contain. The chequer work in the chambers absorbs part of the heat of the burnt gases which eventually make their exit into the outer atmosphere through the stack valve D at the top of the double regenerator. As soon as

the fires in the two generators have attained the necessary high temperature, the air and stack valves are shut, and the steam valve simultaneously opened. The steam, entering the base of the first generator, traverses the fire contained therein in an upward direction. The products (CO_2, CO, H, and some undecomposed steam) passing out at the top traverse in a ∩ direction the two chambers of the 'double regenerator,' after which they enter, in a highly 'superheated' condition, the top of the second generator, through which they pass in a downward direction. In this way, it is claimed, the gases, just prior to leaving the system, come into contact with a bed of highly incandescent carbon, the temperature of which has not been sensibly lowered by the main endothermic steam-carbon interaction, which principally occurs in the first of the two generators. In alternate 'steam blows,' the direction of the steam and gases is reversed, in order to ensure the maximum of uniformity in the working conditions. The plant is operated by means of an interlocking valve gear, which prevents mistakes on the part of the workman. The hot gas produced passes from the bottom of the second generator upwards first of all through the annular 'steam superheater' E (Fig. 17), whereby part of its sensible heat is transmitted to the in-going steam blast, and then through a coke scrubber, where it is cleaned and cooled by a downward water spray. The process works smoothly and is very efficient, the average duration of each air blow being about 70 seconds, and of each steam blow about 5 minutes. The yield of gas, from an average gas coke, is nearly 38 cub. ft., at 0° and 760 mm., per lb. of carbon charged into the generator, about 60 p.c. of which appears in the 'water gas.' The composition of the gas is 3·75 CO_2, 43·70 CO, 45·1 H, 0·5 CH_4, and 6·95 N, its calorific value being about 310 gross and 285 net B.Th.Us. per cub. ft. at 0° and 760 mm. The *ratio* of the net calorific value of the water gas to that of the coke charged into the generators is about 0·70.

With coke at 12*s.* per ton, the cost of making 'blue water gas,' including fuel, wages, interest, and depreciation, is about 4*d.* per 1000 cub. ft., which is equivalent to coal gas at about 8*d.* per 1000 cub. ft.

The most important industrial application of water gas is undoubtedly steel-plate welding, and a large industry has grown up, especially in Germany, for the manufacture of welded steel tubes of large dimensions. The overlapping joint to be welded is heated simultaneously from both sides by special burners (Fig. 18) fed with both water gas and air under pressure, which on mingling produce aërated flames of great heating power. As soon as the joint attains the proper welding heat, it is quickly passed through special rolls which bring about a perfect weld.

Water gas is also used for mixing with ordinary town coal gas, but for this purpose it usually first of all undergoes a process of 'carburetting.' (For the production of 'Carburetted Water gas,' *see* GAS, COAL; *also* GAS, WATER.)

The combustion of gaseous fuels. The following table, relating to the various forms of gaseous fuels described in this article, may be found useful for comparative purposes; the figures for calorific values are approximate only:

Gas	Net. cal. value B.Th.Us. per cub. ft. at 0° and 760 mm.	Vol. air required to burn 1 vol. of gas	Vol. gas + air required per 100 B.Th.Us. cub. ft.	Vol. products incl. H_2O per 100 B.Th.Us. cub. ft.
Blast-furnace gas . .	100	0·715	1·715	1·565
Producer gas	150	1·216	1·480	1·357
Water gas .	290	2·200	1·100	0·953
Coal gas .	590	5·440	1·100	1·050

For information as to the present state of science in gaseous combustion, see article on FLAME (this vol. p. 568) and also report by W. A. Bone to the British Association, Sheffield, 1910. Attention is also drawn to the recent revival of the subject of 'surface combustion'

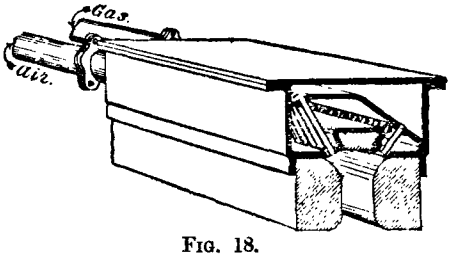


FIG. 18.

by W. A. Bone and C. D. McCourt (*vide* Journal of Gas Lighting, April 4 and 11, 1911, and Engineering, April 15, 1911) whereby numerous economies in the industrial application of gaseous fuels (including steam raising by means of blast furnace gas, producer gas, or surplus gas from by-product coking plants) may be realised. W. A. B.

FUKUGI. The Japanese dyestuff fukugi (botanical origin unknown) has, at least until recently, been employed to a considerable extent as a mordant dyestuff. It consists of the wood of a tree, which, when ground, forms an almost colourless powder, the extract of which is sold in the form of brittle rectangular cakes of a yellowish-brown colour.

Fukugetin $C_{17}H_{12}O_6$, the colouring matter, forms minute canary-yellow prismatic needles, melting at 288°–290° (Perkin and Phipps, Chem. Soc. Trans. 1904, 85, 58). It dissolves in alkaline solutions with a yellow colour and gives with alcoholic lead acetate an orange-yellow precipitate, and with alcoholic ferric chloride a brown-black colouration.

Crystalline acetyl and benzoyl derivatives of this colouring matter could not be obtained, but the *bromine compound* $C_{17}H_{10}O_6Br_2$, minute flat needles, m.p. 280°, is readily prepared by the action of bromine on fukugetin in the presence of acetic acid.

Fukugetin dyes mordanted fabrics shades which are almost identical with those given by luteolin:

Chromium	*Aluminium*	*Tin*	*Iron*
Dull orange-yellow	Orange-yellow	Bright yellow	Olive-brown

and resembles this colouring matter in that its alkaline solution is not oxidised on exposure to air. By fusion with alkali, fukugetin gives *phloroglucinol* and *protocatechuic acid*.

The dyeing properties of 'fukugi' are analogous to those of weld. The similarity in shade, indeed, is so marked that, except in point of strength—for fukugi is a stronger dye than weld—it is impossible to distinguish between them. A. G. P.

FULLER'S EARTH. (Fr. *Terre à foulon*; Ger. *Walkerde*.) A term applied to a variety of clay-like materials which possess in common the property of absorbing grease and oil, and hence are used by fullers for cleansing woollen goods. They vary in colour with dull shades of grey, yellowish, bluish, or greenish, and are soft, with an earthy appearance. They are greasy and unctuous to the touch, and do not adhere to the tongue. When a lump of the dried earth is placed in water, it presents a very curious appearance as it crumbles down to a fine powder; and is not plastic like ordinary clays. Mineralogically they appear to be mixtures; some approximate to kaolinite ($Al_2O_3 \cdot 2SiO_2, 2H_2O$) in composition, and many may be referred to the 'smectite' of A. Breithaupt (1841), a greenish-grey clay from Cilly in Styria. A microscopical examination of English fuller's earth, made by G. P. Merrill (The Non-metallic Minerals, 1904), showed the presence of colourless and greenish-yellow particles with very feeble birefringence, ranging from 0·002 to 0·07 mm. in diameter; very little quartz could be detected, although the presence of free silica is suggested by the analyses. The chemical composition varies widely, and is, in fact, no guide to the commercial value of the material, which depends rather on the physical state of aggregation.

The following analyses are of: I, smectite from Cilly, Styria (Jordan, 1849); II, bluish-grey fuller's earth from Nutfield, Surrey (P. G. Sanford, Geol. Mag. 1889, 456, 526), on material dried at 100° with a loss of 27·47 p.c. water; 13·33 p.c. of all the solid constituents except silica, are soluble in acid; III, yellowish fuller's earth from Nutfield, Surrey (P. G. Sanford, 1889), on material dried at 100° with loss of 29·56 p.c. water; 10·73 p.c. solids, soluble in acid; IV, from Fairborn, South Dakota; V, from south-east of River Junction, Florida; VI, from Decatur Co., Georgia (anal. IV–VI by E. J. Riederer, quoted by H. Ries, 17th Ann. Rep. U.S. Geol. Survey, 1896, iii. 880).

	I.	II.	III.	IV.	V.	VI.
SiO_2	51·21	62·81	59·37	58·72	50·70	67·46
Al_2O_3	12·25	6·92	11·82	16·90	21·07	10·08
Fe_2O_3	2·07	3·78	6·27	4·00	6·88	2·49
CaO	2·13	7·40	6·17	4·06	4·40	3·14
MgO	4·89	2·27	2·09	2·56	0·30	4·09
K_2O	—	0·74	0·84	2·11	—	—
Na_2O	—	—	—			
NaCl	—	0·05	0·14	—	—	—
P_2O_5	—	0·27	0·14	—	—	—
SO_3	—	0·05	0·07	—	—	—
H_2O(comb.)	27·89	15·57	13·19	8·10	9·60	5·61
Moisture		—	—	2·30	7·90	6·28
	100·44	99·86	100·10	98·75	100·85	99·15

Fuller's earth occurs as beds in sedimentary rocks belonging to various geological periods, ranging from the Silurian to the Eocene. The most important deposit in England is a bed 8–12 feet in thickness, lying between sandstones in the Lower Greensand division of the Cretaceous system. This is worked in open pits at Nutfield and Redhill in Surrey. Nearer the surface, where oxidised, it is yellowish, but lower down it is bluish in colour. In Somersetshire, Gloucestershire, and Dorsetshire, the 'fuller's earth formation' of geologists, lying between the limestones of the Great Oolite and the Inferior Oolite, consists of a thick deposit of clays and marls, with beds 2–3 feet in thickness of fuller's earth of good quality. This was formerly extensively worked for use in the cloth mills of the west of England, but now is obtained only on the Downs to the south of Bath. Still smaller quantities are yielded by the Lower Greensand strata near Woburn in Bedfordshire.

For many years the English fuller's earth was considered the best, and even now large quantities are exported to America. Recently, however, deposits have been opened up at several places in the United States, chiefly in Florida, and to a lesser extent in Georgia, Alabama, Arkansas, and California. In Gadsden Co., Florida, it occurs as a bed 4–12 feet in thickness in bedded clays and sandy clays.

The English output amounts to about 15,000 tons per annum, whilst double this quantity is now obtained in America. The price at the pits ranges from 25*s*. to 2*l*. per ton. The earth as dug is dried, crushed, and passed through fine sieves of silk or bronze gauze.

Although still largely used for cleaning cloths, scouring yarns, and washing woollens and fine-dyed goods, fuller's earth now finds a more extensive use in the refining of oils,[1] grease, and lard. Mineral oils are decolourised and clarified by allowing the oil to percolate through long cylinders filled with coarser fuller's earth. Vegetable oils, such as cotton-seed oil, are warmed, stirred with 5–10 p.c. earth, and filtered through bags. Small quantities of the finest grades are used for toilet preparations.

References.—J. T. Porter, Properties and Tests of Fuller's Earth, U.S. Geol. Survey, Bull. 315, 1907; H. Ries, Clays, their Occurrence, Properties, and Uses, 2nd ed., New York, 1908. L. J. S.

FULMINIC ACID (Ger. *Knallsaüre*) C:NOH. The acid has not been obtained in a free state. Scholvein (J. pr. Chem. [2] 32, 461) obtained an ethereal solution of the acid by treating sodium fulminate with dilute sulphuric acid, keeping the mixture cool and dissolving the yellow oil thus obtained in ether. Wieland and Hess (Ber. 1909, 1346) have confirmed this statement, and found that the acid rapidly polymerised to meta-fulminuric acid (*v. infra*). Howard first showed that when silver nitrate or mercuric nitrate was treated with alcohol and excess of nitric acid, a crystalline, detonating precipitate, fulminating silver or fulminating mercury, was obtained. Analyses of these substances (Liebig, Ann. Chim. Phys. [2] 24, 298; Annalen, 24, 546; Gay-Lussac, Ann. Chim. Phys. [2] 25, 285; Divers and Kawakita, Chem. Soc. Trans. 1884, 17) show that they are salts of an acid possessing the formula HCNO. The constitution

[1] The selective absorption of fuller's earth is greater for oils of higher sp.gr. and viscosity and for unsaturated hydrocarbons and sulphur compounds (J. E. Gilpin and O. E. Bransky, Amer. Chem. J. 1910, 44, 251).

of this acid has given rise to much discussion. Berzelius wrote fulminating silver as

$$Ag_2O\cdot(AgN)_2\cdot C_4N_2O_3.$$

This formula accounted for the fact that in many of its reactions only half of the metal is separated, also that the double fulminate of potassium and silver detonates as violently as fulminating silver itself, the detonation being attributed to the decomposition of the compound AgN. Laurent and Gerhardt next proposed the constitution $C_2N(NO_2)Ag_2$, assigning the explosive nature of the body to the presence of a nitro group, and the subsequent experiments of Kekulé (Annalen, 101, 200; 105, 279), and Schischkoff (*ibid.* 101, 213) apparently confirmed this view.

Later Kekulé formulated fulminic acid as nitroacetonitrile $CH_2(NO_2)CN$. He based this formula chiefly on two reactions which fulminic acid undergoes. When mercuric fulminate is treated with sulphuretted hydrogen, ammonium thiocyanate is produced, and with aqueous hydrochloric acid, hydroxylamine is the main product. The production of ammonium thiocyanate suggests that in fulminic acid there is a (CN) group, and that the two nitrogen atoms are in different states of combination, which facts fit in with the formula proposed. But of the two nitrogen atoms only one is represented as oxidised and capable of conversion into hydroxylamine, whereas Divers and Kawakita (Chem. Soc. Trans. 1884, 16) have shown that both atoms of nitrogen are so convertible. Schischkoff (Bull. Soc. Chim. 1860, 294) doubled Kekulé's formula. Steiner proposed

$$HO\cdot N:C:C:N\cdot OH$$

as the correct configuration (Ber. 1876, 779); and Scholl formulated fulminic acid as glyoxime peroxide

$$\begin{matrix} CH:N\cdot O \\ | \quad\quad | \\ CH:N\cdot O \end{matrix}$$

In 1894 Nef found that on treating sodium nitromethane with mercuric chloride, mercuric fulminate was produced, and, moreover, that sodium nitromethane, on treatment with aqueous hydrochloric acid, decomposed into formic acid and hydroxylamine, as does fulminic acid (*v. supra*). On these grounds Nef formulated fulminic acid as carbonyl monoxime C:NOH, and represented the production of mercuric fulminate from nitromethane as follows:—

$$CH_3NO_2 \xrightarrow{\text{Alkali}} \underset{\text{Pseudo-modification.}}{CH_2:NO\cdot ONa} \xrightarrow{HgCl_2} \underset{\text{Unstable.}}{(CH_2:NO\cdot O)_2Hg} \xrightarrow{-H_2O} (C:NO)_2Hg.$$

The explosive character of the fulminates is accounted for by the presence of bivalent carbon in the molecule. It was an old observation, first noticed by Liebig, that when mercuric fulminate was treated with hydrochloric acid of a certain strength, prussic acid was evolved, and this fact was long used to support the nitroacetonitrile formula for fulminic acid. But Nef showed that the compound formed was not prussic acid, but chloroformoxime, a compound possessing an odour similar to that of prussic acid.

$$C:NONa+2HCl=CHCl:NOH+NaCl.$$

Hydrochloric acid converts chloroformoxime into hydroxylamine hydrochloride; sodium hydroxide regenerates a fulminate (Nef, Annalen, 280, 263, *et seq.*). Moreover, nitroacetonitrile has been prepared by removing the elements of water from methazonic acid $C_2H_4O_2N_2$, and is found to have none of the characteristic properties of fulminic acid (Steinkopf and Bohrmann, J. pr. Chem. 1910, [ii.] 81, 97, 193; Ber. 1908, 1044). Scholl (*ibid.* 1899, 3492) applied Friedel and Craft's reaction to fulminic acid, and found that on gently warming mercuric fulminate with benzene, aluminium, and aluminium chloride, benzaldoxime is produced, a further confirmation of Nef's carbonyloxime formula. Angelico (Chem. Zentr. 1901, ii. 404) obtained fulminic acid by treating a solution of mercuric nitrate in excess of dilute nitric acid with a concentrated solution of malonic acid and a few drops of sodium nitrite solution. The course of the reaction is as follows:—

$$CH_2(COOH)_2 \rightarrow \underset{\textit{iso}\text{Nitrosomalonic acid.}}{C:NOH(COOH)_2} \rightarrow \underset{\textit{iso}\text{Nitromalonic acid.}}{C(:NOOH)(COOH)_2} \rightarrow \underset{\textit{iso}\text{Nitroacetic acid.}}{CH(:NOOH)(COOH)} \rightarrow \underset{\textit{iso}\text{Nitromethane.}}{CH_2:NOOH} \rightarrow C:NOH.$$

Wieland and Semper (Ber. 1906, 2522) have shown that phenylmethylnitrolic acid readily decomposes into nitrous acid and the unstable benzonitrile oxide.

$$C(C_6H_5)\begin{matrix}NOH \\ NO_2\end{matrix} \rightarrow HNO_2+C_6H_5\cdot C:N:O.$$

Hence, if a similar decomposition occurs in the case of methyl nitrolic acid, the hitherto unknown nitrile oxide H·C:N:O or the products of its decomposition would be obtained. Wieland (*l.c.*) has shown that the products of the decomposition of methylnitrolic acid are fulminic acid, formic acid, and hydroxylamine, the decomposition being analogous to that of chloroformoxime. The unstable nitrile oxide is probably formed first and then undergoes an isomeric change into fulminic acid.

Wöhler (Ber. 1905, 1351) has determined the molecular weight of fulminic acid by means of the sodium salt, which can be prepared in a pure anhydrous state by the action of sodium amalgam on mercury fulminate suspended in alcohol. The numbers obtained by the cryoscopic method and by determining the equivalent conductivities of dilute solutions correspond closely with the numbers required for the monomolecular formula C:NONa.

In the ordinary method of preparing fulminates by the oxidation of ethyl alcohol, the following changes are supposed to occur (Wieland, Ber. 1907, 418):—

$$CH_3\cdot CH_2\cdot OH \rightarrow \underset{\text{Aldehyde.}}{CH_3CHO} \rightarrow \underset{\textit{iso}\text{Nitrosoacetaldehyde.}}{CH(:NOH)\cdot CHO} \rightarrow \underset{\textit{iso}\text{Nitrosoacetic acid.}}{CH(:NOH)\cdot COOH} \rightarrow \underset{\textit{iso}\text{Nitrosonitroacetic acid.}}{NO_2\cdot C(:NOH)\cdot COOH} \rightarrow \underset{\text{Methylnitrolic acid.}}{NO_2\cdot C(:NOH)H} \rightarrow C:NOH.$$

The experimental evidence in favour of the above hypothesis is as follows: Wieland and Theodorovits (Ber. 1905, 1345) found aldehyde to be a more suitable agent than alcohol for the preparation of fulminates, the formation of methylnitrolic acid from *iso*nitrosoacetic acid has been accomplished by Ponzio (Chem. Soc. Abstr. 1903, i. 453), Wieland has prepared mercuric fulminate from methylnitrolic acid (*v. supra*);

and lastly by treating fulminic acid with nitrous acid, Palazzo (Chem. Soc. Abstr. 1907, i. 489) has obtained methylnitrolic acid as one of the products of the reaction.

The older view of Kekulé as to the constitution of fulminic acid has now been finally abandoned, and the carbonyl oxime formula of Nef has taken its place.

Mercuric fulminate or fulminating mercury $(C:NO)_2Hg$. To prepare this substance on a small scale, 3 parts of mercury are dissolved in 36 parts nitric acid of sp.gr. 1·34, without warming. The solution is then poured into a flask capable of containing 18 times the quantity, in which there has been placed 17 parts alcohol of from 90–92 volumes p.c. The liquids are well mixed, poured back into the first vessel, which is of the same size, shaken to absorb nitrous fumes, and the whole then allowed to stand. In a short time gas is given off and a highly refracting liquid separates at the bottom of the flask. On shaking the flask to mix this liquid with the rest, the whole becomes black, metallic mercury separates, and a violent reaction takes place, which is moderated by the gradual addition of 17 parts of alcohol. Crystals of mercuric fulminate separate on cooling (Liebig).

On a large scale 1 part mercury is dissolved in 10 parts nitric acid of sp.gr. 1·33, and to every kilogram of acid 1 litre of alcohol of sp.gr. 0·833 is added. The reaction begins either spontaneously or on slightly warming. The operation is carried out either in a tubulated retort, in which case the evolved gases escape into a flue, or in glass balloons placed in an open wooden shed. After the alcohol has been added, the operator does not approach the shed till the reaction is complete (*v.* Explosives).

Another method is as follows: 35–40 grams of granular zinc and 4·5 kilogs. of nitric acid (sp.gr. 1·38) are placed in each of fifteen 5-litre glass bottles; when the zinc has dissolved, 500 grams of mercury are added, and the flasks heated until the mercury is dissolved. The contents of the flasks at a temperature of 20°–25° are transferred into a 50-litre retort containing 4·5 kilogs. 91 p.c. alcohol denatured with turpentine and 30 grams of copper nitrate solution. The temperature rises, white fumes are evolved, and mercury fulminate is precipitated. When the white fumes have almost disappeared and a yellowish-red gas is visible, the contents of the retorts are transferred to a large jar into which cold water is poured. The mercury fulminate is thus completely precipitated; it is then filtered, washed with 82–85 p.c. alcohol until the filtrate shows no turbidity on the addition of water, and then with water until neutral to litmus. The fulminate is next placed in a large glass tube 25 cms. wide and 20 cms. long, closed at one end with silk gauze, having 100 meshes per sq. cm. This is shaken in a large vessel containing about 30 litres of water, whereby the fulminate passes through and the foreign matter remains behind. The fulminate in portions of 1·5 kilogs. is rubbed into a fine powder with a wooden pestle in a porcelain dish in the moist state, the finely divided fulminate being collected in earthenware jars. After standing for two days, the fulminate has settled, and the excess of water can be removed, leaving the solid with a constant moisture content of about 15 p.c. (Hagen, Z. Ges. Scheiss- und Sprengstoffw. 1911, 6. 4, 28, 44).

Mercuric fulminate may also be produced by using mercuric oxide for mercury in the above preparation; by boiling silver fulminate with mercury and water, or by precipitating the zinc salt with mercuric chloride. Wöhler and Theodorovits (Ber. 1905, 1345) state that mercuric fulminate is also formed when mercuric nitrate in dilute nitric acid is mixed with methylal, acetal, or lignone obtained by the dry distillation of wood, but the acid must contain nitrous fumes.

It crystallises from hot water in white or greyish silky needles of sp.gr. 4·42; its formula is $(C:N\cdot O)_2Hg,\frac{1}{2}H_2O$; by carefully regulating the temperature and the amount of alcohol, it can be obtained anhydrous. It is insoluble in cold water.

When heated to 180° or when forcibly struck, mercuric fulminate detonates with great violence. The electric spark, or the spark from flint and steel, or contact with nitric or sulphuric acids also bring about explosive decomposition. When moist it may be handled without danger, and when heated to 100° it does not explode if the crystals contain no enclosed mother liquor. The disruptive force of the explosion within a small space is greater than that of gunpowder, but too sudden for its use in guns. The pressure exerted by the gases evolved in the decomposition of the fulminate is less than that caused by the explosion of an equal weight of guncotton, the greater action of the former being attributed to the density of the compound and the great rapidity of the decomposition. Fulminate of mercury is used in the manufacture of percussion caps and of the various detonators used for exploding guncotton, dynamite, and other nitro-glycerin compounds (*v.* Explosives).

Concentrated hydrochloric acid reacts with perfectly dry mercuric fulminate to produce formic acid and hydroxylamine hydrochloride. Thus:

$$C:NOH+2H_2O=H\cdot COOH+NH_2\cdot OH.$$

If the acid be dilute and of a certain strength, chloroformoxime is produced (*v. supra*).

Moderately dilute sulphuric acid decomposes mercuric fulminate without explosion; hot nitric acid converts it into mercuric nitrate, acetic acid, and carbon dioxide. If sulphuretted hydrogen be passed through ether in which mercuric fulminate is suspended, ammonium thiocyanate is formed (*v. supra*); but if the system is kept free from moisture, nitrothioacetamide

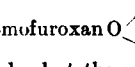
$$CH_2(NO_2)CS\cdot NH_2$$

is also produced, and is decomposed by a further quantity of sulphuretted hydrogen into ammonium thiocyanate, oxalic acid, and sulphur (Steiner, Ber. 1874, 1244; 1875, 518; 1879, 779). Heated with aqueous ammonia, mercuric fulminate yields urea, guanidine, and complex nitrogenous substances; with alcoholic ammonia fulminuric acid is the main product (Steiner).

Potash, lime, and strontia decompose mercuric fulminate on boiling, with the separation of mercuric oxide and the formation of double salts, which detonate on percussion (Liebig).

Finely divided zinc, copper, or silver (the last in contact with platinum) displace mercury from the fulminate, forming salts of zinc, copper,

or silver. Mercuric fulminate readily forms double salts with potassium cyanide and potassium and ammonium thiocyanates (Steiner).

Bromine reacts with mercuric fulminate to produce first of all the unstable additive compound $(CBr_2:N{\cdot}O)_2Hg$, which loses mercuric bromide, giving the unstable bromoformonitrile oxide , two molecules of which polymerise to form dibromofuroxan  . Chlorine reacts similarly, but the oxidising power of the halogen is so strong as to completely destroy the molecule, with the evolution of carbon dioxide (Wieland, Ber. 1909, 4192).

Silver fulminate, *Fulminating silver*

C:NOAg.

In preparing this substance 1 part silver is dissolved in 20 parts nitric acid of sp.gr 1·36 and 27 parts of 86 p.c. spirit of wine added, and the whole gently heated till it froths up. The liquid is then removed, and 27 parts or more of spirit added in order to moderate the action. Silver fulminate separates out on cooling (Liebig).

Silver fulminate is not formed, as was stated by Liebig (Annalen, 5, 287), when nitrogen trioxide is led into an alcoholic solution of silver nitrate (Divers and Kawakita, Chem. Soc. Trans. 1884, 27), and is only produced by the energetic oxidation of alcohol by nitric acid in presence of silver nitrate. Great caution must be exercised in the preparation of this substance. Capacious vessels must be used, so that the liquid may not boil over, as in that case the salt might dry on the outside and then explode; all flame must be kept at a distance, lest the vapours should take fire; and the mixture should be stirred with wooden rods, not with glass rods or other hard bodies. When dry it should be transferred on paper shovels, and kept in paper or cardboard vessels, loosely covered, to prevent explosion from the friction of stoppers or lids.

Silver fulminate crystallises in white opaque glistening needles, scarcely soluble in water, and having a bitter metallic taste. Given in certain doses, it produces violent convulsions (Pagot-la-Forêt), while in doses of 0·3 gram it acts as a narcotic (Ittner).

Silver fulminate is an exceedingly dangerous body, as it explodes much more violently than the mercury salt, by the action of heat, by the electric spark, by friction or percussion, or by contact with oil of vitriol. It even explodes in the moist state, sometimes under water, by friction with a glass rod. It may be rubbed to powder in a mortar with the finger or with a cork. The light accompanying the explosion, which is best seen in the dark, is reddish-white with a tinge of blue (Liebig). When ignited under a pressure of about 2 or 3 mm., it burns slowly with a visible flame. If silver fulminate be thrown into a bottle containing chlorine, it deflagrates before it reaches the bottom, and does not fracture the bottle (E. Davy). Silver fulminate dissolves in hot aqueous ammonia, and the solution, on cooling, deposits crystalline grains of ammonium silver fulminate

$(C:NO_2)(NH_4)Ag$.

This salt is sparingly soluble in water, and explodes with much greater violence than the silver salt, even under liquid, when touched with a glass rod (Liebig). Aqueous solutions of the hydroxides of the metals of the alkalis or alkaline earths, or of the sulphides or chlorides of the alkalis, yield similar double salts when boiled with silver fulminate. Copper or mercury can displace silver wholly or in part from silver fulminate. Zinc, even on boiling for several days, displaces only half of the silver, forming silver-zinc fulminate. The normal zinc salt is prepared by the action of zinc on mercuric fulminate. By acting on this salt with baryta water, and exactly precipitating the barium from the zinc barium fulminate thus produced with sulphuric acid, zinc hydrogen fulminate is obtained. By saturating this salt with metallic bases, many double salts of zinc fulminate are obtained.

Fulminic acid gives rise to a series of polymerisation products. If mercuric fulminate is boiled with ammonium chloride, a salt of fulminuric acid is formed, as was discovered by Liebig. When the ethereal solution of fulminic acid is allowed to stand, metafulminuric acid, a triple polymer, is produced. When metafulminuric acid is warmed with water, it yields cyan*iso*nitrosoacethydroxamic acid, and the latter can be converted into the *iso*fulminuric acid of Ehrenberg, the constitution of which is still unknown. Finally, on long standing metafulminuric acid changes into the *β-iso*fulminuric acid of Scholvein.

FULMINURIC ACID $C_3H_3N_3O_3$. This compound was discovered independently by Liebig (Annalen, 95, 282) and Schischkoff (*ibid.* 97, 53; 101, 213). It is produced by boiling a solution of a metallic chloride or iodide with water and mercuric fulminate

$$4C:NOH+H_2O=C_3H_3N_3O_3+CO_2+NH_3.$$

60–75 grams of well-washed mercuric fulminate are boiled with 700–800 c.c. of water, 60 c.c. of a saturated solution of ammonium chloride are then added, and the whole heated to the boiling-point. As soon as a yellow deposit of oxydimercuric ammonium chloride separates, the flame is removed, and ammonia added till all the mercury is precipitated. On filtering, evaporating the filtrate, and recrystallising the first crop of crystals, pure ammonium fulminurate is obtained. By converting this into the basic lead salt by treating with lead acetate and then precipitating with sulphuretted hydrogen, an aqueous solution of fulminuric acid is obtained. This, on evaporation and standing in a warm place, solidifies to an indistinctly crystalline mass, which, dissolved in alcohol, deposits on evaporation colourless prisms of fulminuric acid. The potassium or ammonium salt may be converted into the silver salt, which may be decomposed by hydrochloric acid, yielding free fulminuric acid. Another method of preparing fulminuric acid is that of Ulpiani (Gazz. chim. ital. 1905, iii. 357). Succinamidedinitrosoperoxide, obtained by the action of fuming nitric acid on ethylacetoacetate and subsequent treatment with concentrated ammonia, yields an acid which Ulpiani has proved to be identical with the fulminuric acid of Liebig, and also *β-iso*fulminuramide. The latter yields *β-iso*fulminuric acid on hydrolysis. Fulminuric acid

decomposes on heating with a slight deflagration at 145° (Steiner, Ber. 1872, 381), and by heating with dilute acid or alkalis decomposes into oxalic acid, ammonia, and carbon dioxide. It appears to be monobasic. The constitution of fulminuric acid is still uncertain. Nef regards it as nitrocyanoacetamide $\begin{matrix}CN\cdot CH\cdot NO_2\\ |\\ HO\cdot C{=}NH\end{matrix}$ (Annalen, 280, 329); while Ulpiani (*l.c.*) represents it as *iso*nitrocyanoacetamide $\begin{matrix}CN\cdot C:NO_2H\\ |\\ O:C{-}NH_2\end{matrix}$.

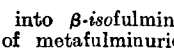
Ammonium fulminurate forms anhydrous monoclinic crystals, which blacken on heating and give off hydrocyanic acid, ammonia, and cyanic acid, which latter partially unite to form urea (Liebig).

Potassium fulminurate. To prepare this salt two parts of mercuric fulminate are gradually added to a saturated solution of one part of potassium chloride, and the mixture gently boiled till the whole is dissolved. The liquid is filtered through a hot funnel from a yellowish precipitate which appears, and the compound of mercuric oxide and potassium fulminurate, which separates in the filtrate, is freed from mercury by sulphuretted hydrogen. On recrystallising from water, potassium fulminurate separates in long glistening prisms, which decompose with incandescence when heated to 225° (Schischkoff).

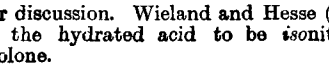
Silver fulminurate may be obtained by heating ammonium or potassium fulminurate with silver nitrate. It is almost insoluble in cold water, but may be recrystallised from boiling water in long very thin needles. Heated with concentrated hydrochloric acid in sealed tubes, at 110°, traces of the oxides of carbon are produced; one-third of the nitrogen goes to form hydroxylamine hydrochloride, and the other two-thirds ammonium chloride (Ehrenberg). Under ordinary pressures at 100° the action is complicated.

The fulminurates of calcium, barium, strontium, iron, and lead may be obtained by double decomposition from ammonium or potassium fulminurates. On heating an ammoniacal solution of copper sulphate with fulminuric acid, dark-blue prisms of ammonium copper fulminurate are deposited on cooling. By passing hydrochloric acid gas through alcohol containing potassium fulminurate in suspension, Schischkoff obtained an oil which he considered to be ethyl fulminurate. This body is, however, not an ethyl salt of fulminuric acid, but has the composition $C_4H_6EtNO_5$. It readily forms additive compounds with ammonia and the amines (Ehrenberg, *l.c.*). According to Siedel (Ber. 1892, 2756), fulminuric acid forms two series of esters, the oxygen ethyl ester melting at 133° and the nitrogen ethyl ester at 155°.

Metafulminuric acid, *Isocyanuric acid* $C_3H_3N_3O_3$. It is obtained by the spontaneous polymerisation of fulminic acid (*q.v.*). It is best prepared by treating chloroformoxime with a small quantity of sodium hydroxide or with aqueous ammonia in the cold (Wieland and Hess, Ber. 1909, 1346). The hydrated acid, containing probably 1 molecule of water, melts at 85°–86°, and the anhydrous acid at 106° with explosion. On long standing, metafulminuric acid changes into *β-iso*fulminuric acid. The constitution of metafulminuric acid is still under discussion. Wieland and Hesse (*l.c.*) consider the hydrated acid to be *iso*nitroso-*iso*oxazolone.



whilst Palazzo and Tamburello (Chem. Zentr. 1907, i. 26) assign to it the constitution



Cyan*iso*nitrosoacetohydroxamic acid $HON:C(CN)\cdot C(OH):NOH$ is obtained by warming metafulminuric acid with water. It is prepared by treating an ethereal solution of chloroformoxime with small quantities of ammonia, until the odour of the latter remains. The ammonium salt is decomposed with hydrochloric acid, and the acid, which crystallises from ether in colourless cubes, melts at 117°–118° (Nef, Annalen, 280, 324).

***Iso*fulminuric acid** $C_3H_3N_3O_3$ of Ehrenberg is obtained by treating cyan*iso*nitrosoacetohydroxamic acid with ammonia. It is a powder, and chars without melting when heating (Nef, *l.c.*; Ehrenberg, J. pr. Chem. [2] 30, 55).

***β-Iso*fulminuric acid** was obtained by Scholvein (*ibid.* [ii.] 32, 461). He treated sodium fulminate with dilute sulphuric acid, and allowed the metafulminuric acid thus formed to stand for some time. Ulpiani (Gazz. chim. ital. 1905, iii. 35, 7) obtained the amide of this acid by treating succinamidedinitrosoperoxide with concentrated ammonia. The amide has the constitution $\begin{matrix}NH_2\cdot C:N\\ |\\ NH_2CO\cdot C:N\end{matrix}\!\!>O$, and the acid is obtained from it by hydrolysis. When anhydrous, the acid melts at 196° with decomposition; the hydrated acid melts at 188°.

FUMARIC ACID and MALEIC ACID

$$\begin{matrix}H\cdot C\cdot COOH\\ \|\\ COOH\cdot C\cdot H\end{matrix} \quad \text{and} \quad \begin{matrix}H\cdot C\cdot COOH\\ \|\\ H\cdot C\cdot COOH\end{matrix}$$

These two unsaturated acids are regarded as stereoisomers, and because of the readiness with which maleic acid forms an anhydride, maleic acid is represented as the *cis-* modification, and fumaric, which forms no anhydride, as the *trans-* modification. (For further details, *v.* Organic Chemistry for Advanced Students, Cohen, iii.) These two unsaturated dibasic acids may be obtained by heating malic acid:

$$\begin{matrix}CH(OH)\cdot COOH\\ |\\ CH_2\cdot COOH\end{matrix} = C_2H_2(COOH)_2 + H_2O;$$

maleic anhydride $C_4H_2O_3$ distils over, and fumaric acid remains behind in the retort. By rapid distillation at 110°–140°, maleic anhydride is obtained as chief product; by long heating to 150°, fumaric acid is mainly formed.

Both acids when treated with nascent hydrogen yield succinic acid. Both unite with hydrobromic acid to form monobromsuccinic acid. But fumaric acid unites with bromine to form dibromosuccinic acid, whilst maleic acid gives *iso*dibromosuccinic acid. Potassium permanganate oxidises fumaric acid to racemic acid; maleic acid is converted into mesotartaric acid.

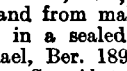
Fumaric acid is much less soluble in water than maleic acid.

Fumaric acid occurs in various plants, as in the common fumitory (*Fumaria officinalis* [Linn.]), in *Corydalis bulbosa*, *Glaucium flavum*, (Crantz), *Cetraria islandica* (Ach.), and in varieties of *Agaricus*. It can be prepared by heating halogen substituted succinic acids (Brunner and Chuard, Ber. 1897, 201; Swarts, Zeitsch. Chem. 1868, 25), and from maleic acid (*v. infra*). When heated in a sealed tube it melts at 286°–287° (Michael, Ber. 1895, 163); sp. gr. 1·625 (Tanatar, Chem. Soc. Abstr. 1893, i. 11), It crystallises in small prisms, which sublime at 200° without decomposition, but by distillation is converted into maleic anhydride and water. Fumaric acid forms no anhydride of its own; all processes of dehydration convert it into maleic anhydride, which unites with water to form maleic acid.

Maleic acid has never been found to occur in nature, and is best obtained by heating malic acid with acetyl chloride, and decomposing the acetyl maleic anhydride into maleic anhydride and acetyl chloride, and then heating the anhydride with water. It can also be prepared by heating fumaric acid (*v. supra*). It forms large prisms or tabular crystals, very soluble even in cold water, m.p. 130°, b.p. 160°, decomposing for the most part into anhydride and water. Maleic acid is converted into fumaric acid when it is heated for some time at 130° or in sealed tubes at 200°, when it is treated in the cold with dilute mineral acids and certain organic acids, with sulphuretted hydrogen followed by sulphur dioxide, or with bromine in sunlight. By heating the esters of maleic acid with iodine, the esters of fumaric acid are produced.

Maleic anhydride is a white crystalline solid, melting at 56° and boiling at 196°.

FUNGICIDES *v.* DISINFECTANTS and PLANT-SPRAYS.

FURFURAL, *Furfurol*, *Furfuraldehyde*, *Pyromucic aldehyde* $C_5H_4O_2$,  first obtained by Döbereiner by distilling sugar with manganese dioxide and dilute sulphuric acid. It may be prepared in small yields by heating sugar with dilute tartaric or lactic acids, or simply by heating with water; hence it occurs in brewers' wort and sometimes in the finished beer, also forming a constituent of fusel oil from the distilleries. Is produced during the heating of madder with dilute sulphuric acid in the preparation of garancin; during the dry distillation of oak timber; and by heating starch at 200°. It is a constituent of many essential oils (Schimmel). Best prepared by distilling bran with dilute sulphuric acid and fractionating the distillate.

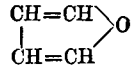
Colourless liquid; b.p. 161°; smelling of oil of bitter almonds and oil of cinnamon; sp.gr. 1·1594 at 20°/4°; $\mu a = 1{\cdot}5186$; soluble in 11 parts of water at 13°.

Reduces silver oxide with formation of pyromucic acid. Shows a striking similarity to benzaldehyde in its reactions, forming furfuralcohol and pyromucic acid with caustic potash, furfoïn with potassium cyanide, dyestuffs with derivatives of aniline, &c.

The *urethane* is a very characteristic derivative, crystallising in needles, m.p. 169°, which may be sublimed. The *semicarbazone* melts at 202°–203°.

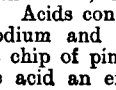
Owing to the presence of furfurol in beer and spirits, many methods have been devised for its detection. One of the most sensitive tests is with colourless aniline, absolute alcohol, and either hydrochloric or glacial acetic acid, a cherry-red colouration being produced, the amount of furfurol present being estimated by the depth of colour (J. Amer. Chem. Soc. 1906, 1629). Other methods of estimation are: precipitation with phloroglucin and hydrochloric acid (Weibel and Zeisel), and the preparation of the insoluble semioxamazide.

FURFURAN, *Furan*, *Tetrol*, *Tetraphenol*



Is a fairly stable ether compound, obtained by the distillation of the barium salt of pyromucic acid with soda-lime; by the distillation of calcium succinate; or by heating succinic dialdehyde with water at 180°. Best prepared by heating pyromucic acid alone in a tube at 260°–275°, as the barium salt produces also the hydrocarbon C_3H_4 and CO (Freundler, Compt. rend. 124, 1157).

Appears to be contained in the volatile portions of pinewood tar. Colourless liquid, boiling at 32°; insoluble in water, readily soluble in alcohol and ether. Acids convert it into pyrrole-red; metallic sodium and alkalis do not attack it. Colours a chip of pinewood moistened with hydrochloric acid an emerald green.

By nitration in presence of acetic anhydride, a monoacetin of nitrosuccinicaldehyde is formed, which reacts with pyridine, producing nitrofurfuran; m.p. 28°; 

FURFURINE $C_{15}H_{12}N_2O_3$. Prepared from furfural by first making the amide with the aid of ammonia. Furfuramide is boiled for 15 minutes with very dilute caustic potash, and the furfurine which separates is dissolved in excess of boiling dilute oxalic acid. The so-formed dioxalate is collected, and again dissolved in 100 parts boiling water, and precipitated with ammonia (Bahrmann, J. pr. Chem. [2] 27, 313); white needles; m.p. 116°; very sparingly soluble in cold water, but appreciably soluble in hot; readily soluble in alcohol or ether. It is a mono-acid base, and the crystals turn brown in moist air. Expels ammonia from boiling solutions of ammonium salts, but is itself precipitated by ammonia from its salts in the cold.

When heated with sodium, *iso*furfurine is formed. Forms a nitrosamine $C_{15}H_{11}(NO)N_2O_3$ by acting on the sulphate with very dilute potassium nitrite, and this exists as golden triclinic crystals; m.p. 112° (Schiff, Ber. 11, 1250).

FURFUROIDS are a group of compounds closely related to the pentoses and pentosans, distinguished by yielding furfural as a characteristic product of decomposition on treatment with acids (Cross, Bevan and Smith, Chem. Soc. Trans. 1897, 1001).

FURFUROL *v.* FURFURAL.

FURNACES FOR GENERAL LABORATORY USE. Fig. 1 shows a Fletcher's gas muffle furnace affording high temperatures without an air blast. With the use of a suitable pressure governor, fairly constant temperatures may be obtained. The furnace can be used for heating precipitates, fusions, roasting of ores, and similar laboratory operations. When crucibles

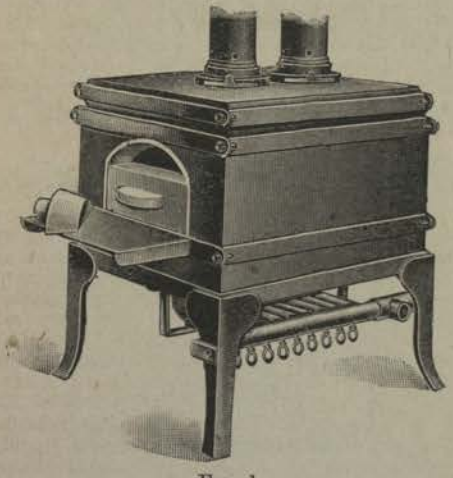


FIG. 1.

which have to be weighed are heated, a sheet of asbestos cloth should be placed on the floor of the muffle.

A Fletcher's muffle furnace (Fig. 2), in which petroleum is used as fuel, is designed for use where gas is not available. With the burner shown, the necessary air-blast may be obtained by a foot blower; or an automatic petroleum

FIG. 2.

burner may be used, which dispenses with the use of an external supply of compressed air.

Fig. 3 shows a Fletcher's injector furnace, which is efficient and rapid in working. For ordinary purposes, a foot blower is used, but for very high temperatures a blower driven by power is preferable. Cast iron can readily be fused in this furnace.

A furnace of similar shape to that shown in Fig. 3, but with a modified burner, is used where extremely high temperatures are required, a stream of oxygen being employed instead of the usual air blast. In order to prevent the

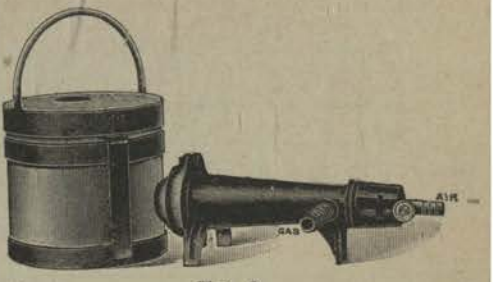


FIG. 3.

perforation of crucibles by a small but extremely hot flame, the burner is so designed that the oxygen is mixed with air before it enters the furnace, a more diffused flame being thus obtained.

An exceedingly useful furnace designed by Fletcher is shown in Fig. 4 (*a* and *b*). This furnace works either as a draught or blast furnace with the same burner, and may be used for any temperature up to the fusing-point of the casing. It is adapted for crucibles, muffles, tubes, cupels, distillation by descension, treatment of refractory substances with gases at high temperatures, small forgings, roasting of ores, &c. When used as a blast furnace as shown in the figure, an empty crucible can be raised to the fusing-point of cast iron in 2

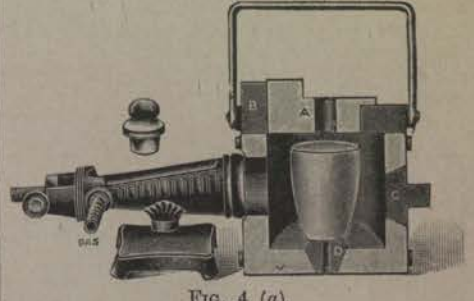


FIG. 4 (*a*).

minutes, starting all cold. For use as a draught furnace, the plug C is removed and replaced by a chimney, when a crucible may be heated to bright redness in 10 minutes. The furnace may also be turned on its side, when the doors A and B become the front of a muffle furnace.

A furnace in which magnesia is used as the refractory material, and designed to employ the oxygen-coal gas flame is made by Merck. The burner is provided with a water jacket; and the mixed gases, which are projected through the bottom of the furnace, are so directed that the flame does not play directly on the substance in the crucible. The employment of magnesia for the parts most exposed to the flame, admits of the use of a very high temperature.

Fig. 5 shows a Fletcher's reverberatory furnace available for all general laboratory

work, and capable, when working with a draught, of producing a clear yellow heat above the fusing-point of fine silver, and when worked with a blast, for which the same burner is employed, of melting cast steel. It may be employed as shown, or one or both doors may

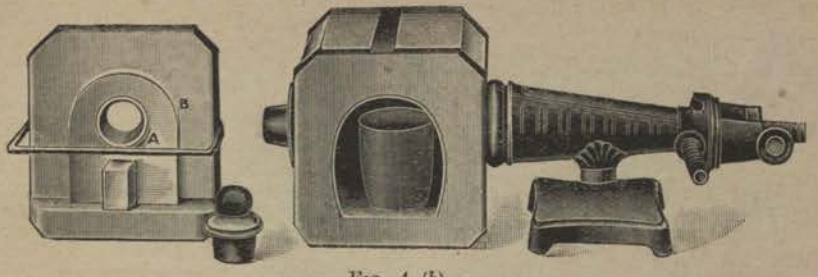


FIG. 4 (*b*).

be arranged to receive a muffle, so that the furnace may be used for muffle or crucible operations, or for both simultaneously. Perrot's furnace for heating crucibles by gas is described fully in Bull. Soc. chim. 1867, 7, 332.

FIG. 5.

A furnace designed by Rössler (Zeitsch. anal. Chem. 1886, 95, Dingl. poly. J. 253, 79; J. Soc. Chem. Ind. 1884, 512) for intensely heating small crucibles employed in chemical analysis is shown in Fig. 6. Cold air, admitted in carefully regulated quantity at *e* to the burner *a*, becomes heated during its passage around a jacket, *d*. Combustion takes place within a muffle, *c*, surrounding the crucible *b*, and the combustion products pass out through the cover of the muffle and through a chimney, *g*, the draught in which is assisted and regulated by a second burner. A somewhat similar arrangement has been described by Hempel (Zeitsch. anal. Chem. 1877, 454).

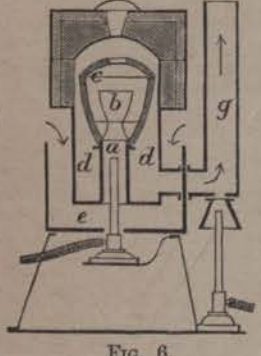


FIG. 6.

Fig. 7 shows a Fletcher's furnace, which, although primarily designed for organic analysis, will be found very useful for many other laboratory operations. The burners are placed in front of the furnace, and clear from all falling dirt, and since these are made of brass, there is no ironwork to rust. The furnace is made in 6-inch sections, and can, therefore, be built up to any length. The body of the furnace is made entirely of fire-clay.

Sefström's portable furnace for use with charcoal is shown in Fig. 8. It consists of an outer cylinder forming an air chamber around

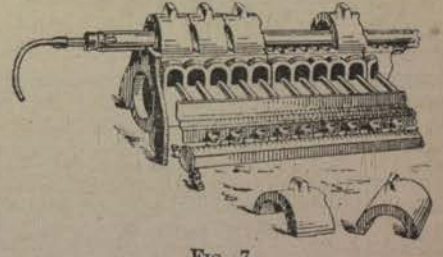


FIG. 7.

a cylinder, *b*, fixed in position by a flange, *g*. The cylinder *b* is perforated with holes containing small tapering nozzles, *e*, and is lined with fire-clay shaped as shown. When greater space is required for fuel, &c., a hoop, *h*, may be placed around the top of the cylinder *b*. It consists of a strip of sheet iron, in one end of

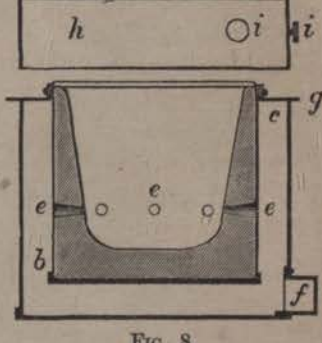


FIG. 8.

which are two holes, *i*, whilst in the other end is a button which may be inserted in either of the holes, so that the hoop may fit over the cylinder *b*, or, when not in use, over the outer cylinder. The blast is supplied at *f* by a small bellows.

The electric furnace shown in Fig. 9 is specially adapted for fusions on a small scale,

and for the production of high local temperatures. The process can be watched from beginning to end through the mica doors, the eyes being protected by blue spectacles. The furnace consists of an iron muffle lined with

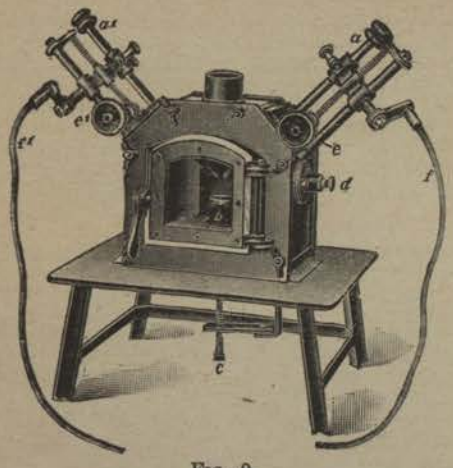


FIG. 9.

fire-clay. The block *b* can be raised or lowered by means of the set-screw *c*. On this block stands the crucible, made of lime, magnesite, &c., according to the purpose required. The cables *f* and *f'* convey the current to the electrodes, *a* and *a'*, which can be adjusted by means of the regulating wheels *e* and *e'*. The mica doors permit of easy access to the interior of the furnace. In this type of furnace the heat is generated in a chamber of practically non-conducting material, and since no cold gases are introduced, extremely high temperatures may be produced in the crucible.

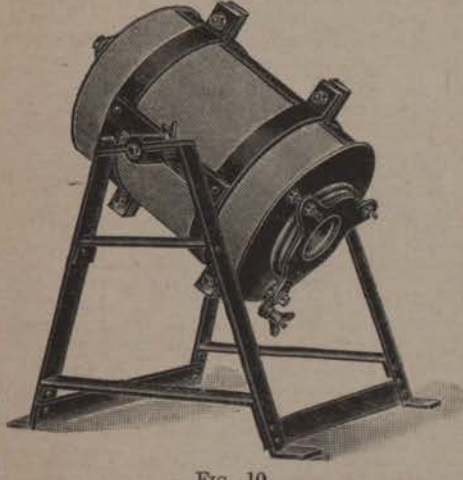


FIG. 10.

In the tube furnace shown in Fig. 10, the heating body consists of a tube of highly refractory porcelain, around which is coiled a ribbon of very thin platinum, which makes a closer contact with the porcelain and lasts much longer than platinum wire. A temperature of 1400° can easily be reached, but above this the procelain begins to conduct electricity, and an electrolytic action is set up between the platinum and the tube, which will eventually cause breakage. In the figure the furnace is shown mounted on a tilting frame for use in any position. It may be obtained wound for any supply between 65 and 250 volts. In using the furnace it is necessary to pay attention to the following points: (1) No cold object must be brought into contact with the tube while it is incandescent. (2) The furnace should not be kept at its maximum temperature longer than is necessary. (3) A suitable resistance should be connected up with the furnace in order to ensure gradual heating, and to provide a means of regulating the temperature.

Fig. 11 shows an electrically heated crucible furnace, in which the heating resistance consists of platinum wire embedded in a suitable fire-clay. The furnace is designed for crucibles of

FIG. 11.

a capacity not exceeding 30 c.c., and the temperature obtained is about 1050°–1100°. Inside the furnace the crucible rests upon a small stand of refractory porcelain; but if the contents of the crucible are moist, and it is required to heat them slowly, the crucible is suspended in such a way that only the lower part is within the furnace. For quantitative work, the furnace cover can be coated with platinum foil in order to prevent chips of fire-clay from falling into the crucible, and in special cases the whole of the interior may be so lined. The temperature obtained is more uniform than that produced by the gas blow-pipe, and the use of this furnace entirely prevents the damage, which, particularly in the analysis of phosphates, is caused by the reducing gases, to a platinum crucible heated by gas. The consumption of current at 110 volts is 2·3 amperes, and the platinum resistance has an average life of about 850 burning hours.

A crucible furnace in which the heat is generated by the passage of an electric current through a resistance of granular carbon, is made by Merck (Fig. 12). In order to withstand very

high temperatures, the parts most exposed to the heat are made of magnesia, which is also used as a packing to minimise loss of heat.

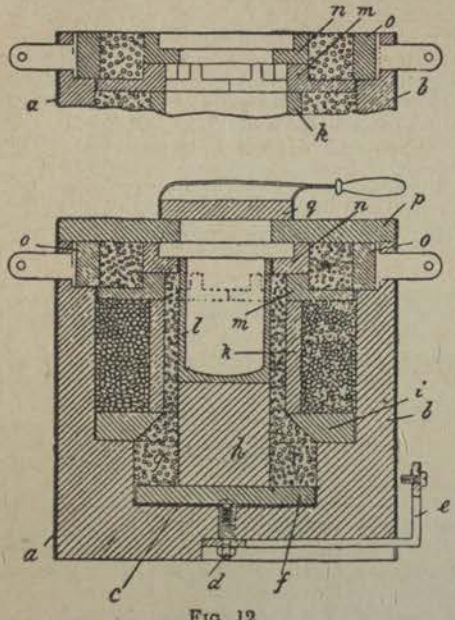


FIG. 12.

a, *b*, Case; *c*, copper plate; *d*, bolt; *e*, terminal; *f*, carbon block; *g*, resistance; *h*, crucible stand; *i*, magnesite ring; *l*, heating chamber; *m*, *n*, rings of magnesia; *o*, annular electrode; *p*, large cover; *q*, small cover.

When using the maximum amount of energy (about 8000 watts), the temperature approaches the melting-point of corundum.

An electrically heated tube furnace (Fig. 13) is described by Blount (Analyst, 1905, 30, 29), in which the resistance consists of loosely packed retort carbon mixed with a suitable quantity of siloxicon. The essential parts of this furnace are two concentric fire-clay tubes, surrounding, but not actually touching, that part of the porcelain tube to be heated. The resistance material is packed between these two fire-clay tubes, the current being led in by means of an annular copper disc at each end, which is provided with a short cylindrical projection fitting closely

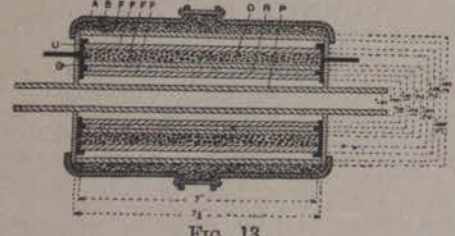


FIG. 13.

A, clamps; B, asbestos cloth; C, copper terminals; F, fire-clay tubes; D, pieces of fire-clay; R, resistance mixture; P, porcelain tube; U, uralite discs.

in between the two tubes so as to make good contact for the resistance material. The two tubes which form the furnace proper are surrounded by two other wider fire-clay tubes which serve merely to insulate the heat. They may be covered with asbestos wrapping still further to retain the heat. The ends of the furnace are made of uralite discs, which also support the tube to be heated. With this apparatus, a piece of copper weighing from 15 to 20 grams can be fused in about 18 minutes.

For temperatures up to 2100°, electrically heated furnaces are made in which a current of 500 amperes and 5 volts is led through a thin-walled tube of pure iridium, but the extremely high price of this metal greatly limits the use of these furnaces.

Furnaces employed for particular purposes will be found described under special headings, as ASSAYING; ALUMINIUM; &c., &c.

FURUNCULINE *v.* SYNTHETIC DRUGS.

FUSEL OIL. *Fermentation amyl alcohol, Potato oil, Grain oil, Marc brandy oil.* (Ger. *Fuselöl*; Fr. *Huile de pommes de terre.*) The mixture of alcohols constituting this substance is produced in comparatively small quantity in the alcoholic fermentation of most bodies containing sugar, the largest proportion being contained in the alcohol prepared from potatos, while in the alcohol from the 'marc' of grapes and from beetroots, grain, &c., smaller quantities are found.

Fusel oil consists mainly of two alcohols, one of which, *iso*-butyl carbinol, or *iso*-amyl alcohol, or inactive amyl alcohol $(CH_3)_2CH{\cdot}CH_2CH_2{\cdot}OH$, is optically inactive, while the other, secondary butyl carbinol or active amyl alcohol

$$C_2H_5{\cdot}CH_3{\cdot}CH{\cdot}CH_2{\cdot}OH,$$

rotates the plane of polarised light to the left sufficiently to render fusel oil strongly lævorotatory. The following alcohols are said to have been separated from fusel oil :—

Ethyl alcohol . .	$CH_3{\cdot}CH_2{\cdot}OH$.
Normal propyl alcohol	$C_2H_5{\cdot}CH_2{\cdot}OH$.
*iso*Propyl ,,	$(CH_3)_2CH{\cdot}OH$.
Normal butyl ,,	$C_3H_7{\cdot}CH_2{\cdot}OH$.
*iso*Butyl ,,	$(CH_3)_2CH{\cdot}CH_2{\cdot}OH$.
Tertiary butyl ,,	$(CH_3)_3C{\cdot}OH$.
Active amyl ,,	$C_2H_5(CH_3)CH{\cdot}CH_2{\cdot}OH$.
Inactive amyl ,,	$(CH_3)_2CH{\cdot}CH_2{\cdot}CH_2{\cdot}OH$.
Methyl normal propyl carbinol . .	$CH_3(C_3H_7)CH{\cdot}OH$.
Normal primary amyl alcohol . .	$C_5H_{11}{\cdot}OH$.
A primary hexyl alcohol	$C_6H_{13}{\cdot}OH$.
,, heptyl ,,	$C_7H_{15}{\cdot}OH$.

Formic, acetic, propionic, butyric, valeric, caproic, œnanthic, caprylic, pelargonic, and capric acids have been found in fusel oils, and ethyl acetate and other esters and various aldehydes are also present.

The composition of fusel oil depends on the source of production, the nature of the ferments (*vide infra*), and the method of distillation. That from grain or potatos consists largely of amyl alcohols with ethyl alcohol, the inactive amyl alcohol being the principal constituent. The fusel oil prepared in the South of France from the marc of brandy contains normal propyl alcohol in considerable quantities, while that obtained from the beet contains a larger proportion of *iso*butyl alcohol. Also the ferment in brewer's yeast (*Saccharomyces cerevisiæ* [Meyer]) appears to favour the production of

*iso*butyl alcohol, whilst *Saccharomyces ellipsoides* (Reess.) (from the grape) tends to produce normal butyl alcohol. Higher alcohols are said to be rapidly produced after fermentation ceases, and, therefore, the higher alcohols tend to increase the longer the interval between fermentation and distillation. This may be due to some organism other than yeast becoming active after the yeast has done its work.

The proportion of fusel oil obtained during fermentation is also modified by the condition of the mash. Alkaline liquids, particularly when warm and containing large quantities of sugar, promote its formation, while acid liquids, especially when containing tartaric, racemic, or citric acids, are said to prevent its production. The presence, in any quantity, of tartar or certain bitters such as that of hops also prevents its formation, so that wines, &c., are usually free from fusel oil. According to Le Bel (Compt. rend. 96, 1368), pure sugar fermented with beer yeast yields less of these alcohols than wine or beer. Obviously a larger proportion of higher alcohols is likely to occur in spirits distilled from a pot-still than when highly rectifying appliances are used, as in patent stills.

Fusel oil is contained principally in the alcoholic distillates commencing to come off at 105°–125° and ending at 132°–137°. Between 105° and 120° most of the *iso*butyl alcohol is obtained, while the amyl alcohols distil principally between 128° and 132°.

According to Rabuteau (Compt. rend. 87, 500), the following represents the percentage by volume of the principal constituents of *potato oil*:—

*iso*Propyl alcohol	15·0
Propyl ,,	3·0
Normal butyl alcohol	6·5
*iso*Butyl ,,	5·0
Inactive amyl ,,	27·5
Active ,, ,,	6·0
Products boiling above 132° and retaining amyl alcohol	17·0
Ethyl alcohol, ethyl acetate, and aldehyde	7·5
Water	12·5
	100·0

Later observations, however, do not confirm Rabuteau's statement that fusel oil contains *iso*propyl alcohol.

According to Ulex, the distillation of fusel oil produced from (1) beet, (2) potatos, (3) grain, gives (roughly) the following percentage by volume:—

	1	2	3
80°–100° (principally propyl alcohol)	13	13	31
100°–130° (butyl and amyl alcohols)	53	30	26
Above 130° (amyl alcohol)	34	57	43

By careful fractional distillation of wine brandy 25 years old, Ordonneau (Compt. rend. 1886, 102, 217) obtained the following substances:—

	P.c. by volume
Aldehyde	0·003
Ethyl acetate	0·035
Acetal	traces
Œnanthylic ester	about 0·004
Propionic, butyric, and caproic esters	0·003
Normal propyl alcohol	0·040
,, butyl ,,	0·218
'Amyl alcohol'	0·0838
Hexyl ,,	0·0006
Heptyl ,,	0·0015
Amine bases (probably of the pyridine series	traces

Commercial alcohols from maize, beet, and potatos, showed the presence, in addition to other substances, of propyl alcohol, active and inactive amyl alcohol, pyridine, a base which appeared to be collidine, and *iso*butyl alcohol, without a trace of normal butyl alcohol. Ordonneau attributes the disagreeable difference in flavour between wine brandy and that from a mash to the presence in the former of normal butyl alcohol, while the latter contains the disagreeably smelling *iso*butyl alcohol, but no normal butyl alcohol. He recommends that the fermentation of a mash should be performed with the elliptic *wine* yeast instead of the globular *beer* yeast, as he finds by experiment that the former produces the normal butyl alcohol, while the latter tends to form the *iso*- variety.

The *iso*-amyl alcohol (inactive amyl alcohol) may be separated from fusel oil by agitation with a saturated solution of common salt. The amyl, butyl, and propyl alcohols, which are less soluble in that medium than in water, separate as an oily layer, while the ethyl alcohol remains in the brine. The separated oil is distilled, the portion coming off between 105° and 120° consisting principally of *iso*-butyl alcohol, while that distilling between 125° and 140° contains the amyl alcohols. This is collected separately, agitated with hot milk of lime, dried over calcium chloride and redistilled, the portion coming off between 128° and 132° being collected separately. In this way the *iso*-amyl alcohol is obtained almost free from butyl alcohol and from valeric aldehyde. The barium amyl sulphate produced from active amyl alcohol is 2½ times as soluble in water as that from the inactive variety, so that these salts may be separated by careful fractional crystallisation, and afterwards treated for reproduction of the alcohols.

The composition of fusel oil from various sources has been carefully studied by Karl Windisch (*v.* Arbeiten aus dem Kaiserlichen Gesundheitsamt, 1892, Bd. 8), his principal results from (1) potato and (2) corn fusel oil, expressed in grams per kilog., and excluding ethyl alcohol and water, being as follows:—

	(1)	(2)
Normal propyl alcohol	68·54	36·90
*iso*Butyl alcohol	243·50	157·60
Amyl ,,	687·60	758·50
Hexyl ,,	—	1·33
Heptyl ,,	—	trace
Free fatty acids	0·11	1·60
Fatty acid esters	0·20	3·05
Furfurol and bases	0·05	0·21
Terpenes	—	0·33
Terpene hydrate	—	0·48

The free fatty acids and acid esters were also analysed with the following results expressed in percentages, the acids and esters being taken together in the potato fusel oil, and separately in the fusel oil from corn:—

	Potato.	Corn	
	Free fatty acids and acids esters	Free fatty acids	Esters
Capric .	36	44·1	40·7
Pelargonic	12	12·9	14·2
Caprylic .	32	26·7	34·8
Caproic	14	13·2	9·6
Butyric .	0·5	0·4	0·4
Acetic .	3·5	2·7	0·3

The terpene $C_{10}H_{16}$, which is present, together with its hydrate $C_{10}H_{18}O$, has not been exactly identified, but it has a close resemblance to phellandrene.

The injurious effect of raw or recently manufactured spirits is attributed (*inter alia*) to the presence of fusel oil produced during the fermentation and not thoroughly separated. Bell considers it to be due rather to furfural and other empyreumatic bodies, and this view is supported by Lauder Brunton, who thinks that the toxic effect of spirit may also be attributed, in some cases, to the presence of traces of alkaloidal bodies, arising from the decomposition of albuminous substances in the mash. Schidrowitz also found in new whisky substances such as pyrrol, phenolic bodies, traces of nitriles, &c., which disappear as the spirit matures (J. Soc. Chem. Ind. June, 1905). The actual adulteration of alcoholic liquors with fusel oil is improbable, but spirits containing 0·3 p.c. of that substance are usually deemed to be injurious, although the general tendency of the evidence given before the Royal Commission on Whisky and Potable Spirits, was to show that the evil effects of spirits is due to the ethyl alcohol itself, rather than to fusel oil or other secondary products present.

Samples of spirits examined by Dupré (Analyst, 1, 6) contained for 100 parts by weight of ethyl alcohol:

Scotch whisky containing 54·5 p.c. of alcohol	0·19 p.c. amyl alcohol
Cape smoke . .	0·24 ,,
Common Samshoe .	0·18 ,,
Fine ,, .	0·13 ,,

According to Le Bel (Compt. rend. 96, 1368), natural white wine contains 0·2 p.c. amyl alcohol per litre, and, according to Hamberg (Schmidt's Jahrb. der Medicin, 201, 27, 1885), beer contains about 0·00114 p.c. of fusel oil.

Beer recommends a maximum permissible limit to the fusel oil in brandy, liqueurs, &c., of 0·3 p.c.; but Bödlander and Traube (Rep. Anal. Chem. 7, 167), who have examined a number of commercial spirits, propose a limit of 0·10 -0·15 p.c.

The separation of fusel oil from spirit is extremely difficult. Among the various substances proposed or used for its destruction or removal, are charcoal, soap, oil, and fatty substances, potash ('grey salts'), pearl ash ('white salts'), lime, sulphuric, nitric, and hydrochloric acids, bleaching powder, and potassium permanganate.

Charcoal, soap, and oil, are supposed to separate the fusel oil unchanged. When rectified over potassium permanganate or bleaching powder, the amyl alcohols are converted into valerates, but a portion of the ethyl alcohol is also decomposed. Bleaching powder, when used, is made into a milk at the ordinary temperature and permitted to digest for a time, after which the spirit is drawn off and rectified. According to Klezensky, if the spirit be distilled from *hard soda soap*, the fusel oil remains with the soap, from which it may be separated by subsequent distillation at a more elevated temperature.

The most approved method of separation, however, is by well-burnt granulated vegetable charcoal or bone-black. The charcoal is placed upon perforated trays in a vessel surrounded by a cooling jacket, and the spirit, usually diluted to about 160°Tr., is caused to pass through several layers. The operation should not be performed above the ordinary temperature, as the fusel oil is again dissolved from the charcoal near the boiling temperature. From 3 to 5 vols. of charcoal are required for the successful treatment of 100 vols. of brandy. The whole of the fusel oil is evolved from the charcoal on treatment by superheated steam, and the charcoal may be repeatedly used after heating to redness to drive off the occluded gases, &c. It is noticeable that the fusel oil obtained by steaming the charcoal does not represent the whole of that removed from the spirit, nor are sufficient compounds which might be produced by the decomposition of the fusel oils found to account for this loss.

Raw brandy, produced in Switzerland from potatos, maize, and the residues from breweries, by the continuous process, has been found to contain 1·32 p.c. of fusel oil. Raw Swiss brandy filtered through charcoal showed 0·2 p.c. of fusel oil; that rectified by distillation, 0·06; and that filtered through charcoal and afterwards rectified contained none. *Cf.* F. Pampe (Chem. Zeit. 11, 313).

Apart from the desirability of removing the excess of fusel oil from spirits intended for human consumption as a beverage, the oil is recovered for its own sake, as a valuable by-product in the manufacture of spirit, its price being at present about 6 times that of ordinary alcohol.

By means of patent stills, the fusel oil may be rapidly and almost completely removed, and with suitable rectifying apparatus, alcohol at 95° and fusel oil may separately be obtained in the proportions of 130 to 1, or nearly 0·8 p.c. (by volume) of fusel oil.

The amyl alcohols of fusel oil dissolve in about 40 parts of cold water. According to Balbiano (Ber. 9, 1437), the inactive variety is soluble in about 50 parts of water at 14°, and is less soluble at 50°. *Iso*butyl alcohol dissolves in 10 parts of water at 15°. One part of inactive amyl alcohol takes up about 0·08 part of water, while *iso*butyl alcohol dissolves nearly twice that amount.

Fusel oil dissolves freely in ether, chloroform, alcohol, benzene, and carbon tetrachloride.

It is largely used for the manufacture of amyl acetate (*v.* ACETIC ACID), which has numerous applications in the arts and manufactures, as flavouring essences (pear oil, &c.), for confectionery, as a solvent for cellulose, and in making lacquers, varnishes, artificial leather, waterproofing, and sanitary sheeting for hospitals, &c. It is also used in toxicology as a solvent for alkaloids, for which purpose it should be carefully purified by agitation with

dilute acid to remove an alkaloidal body which it is liable to contain. On account of its strong affinity for chlorine, fusel oil has been employed in chlorine generators for laboratory purposes as an absorbent for that gas, to prevent its escape into the atmosphere when the supply is no longer required; whilst its principal constituent (amyl alcohol) is employed in the estimation of fat in milk by the centrifugal methods.

Detection of fusel oils.—When a sample of spirit is poured on filter paper or on the hand, and allowed to evaporate spontaneously, the characteristic suffocating odour of fusel oil may be recognised towards the close of the evaporation. So small a quantity as $\frac{1}{2000}$ part of amyl alcohol in gin may thus be detected.

On dissolving 1 gram of caustic potash in 150 c.c. of the spirit, concentrating slowly to 15 c.c., and adding an equal volume of dilute sulphuric acid, a powerful odour is given off, which is frequently sufficiently distinctive to show the nature of the mash from which the spirit was obtained. Betali (Ber. 8, 72) adds to the alcohol 6–7 volumes of water, and agitates with sufficient chloroform to produce a small layer on subsidence. This layer is drawn off and evaporated, and the residue is tested by digestion with potassium acetate and sulphuric acid. In presence of fusel oil the characteristic pear-like odour of amyl acetate is observable.

Marquardt dilutes 40 c.c. of the spirit with sufficient water to raise the density to about 0·980, and agitates the mixture with 15 c.c. of pure chloroform, which, after settlement, is drawn off, shaken with an equal volume of water, and evaporated spontaneously. The residue is treated with a little water, one or two drops of sulphuric acid, and sufficient of a strong solution of potassium permanganate to ensure that the liquid shall remain red after standing for 24 hours in a closed tube. The odour of valeric aldehyde is frequently noticeable shortly after the addition of the permanganate, but the characteristic smell of *valeric acid*, on which this very delicate test is based, is not appreciable until after standing.

Determination.—Fusel oil containing not more than 15 p.c. of proof spirit is allowed to be delivered from distilleries in the United Kingdom or to be admitted on importation from abroad duty free.

Numerous methods have been suggested for the estimation of ethyl alcohol in fusel oil, but none is free from objection. The following method can be recommended as being sufficiently accurate for all practical purposes.

75 c.c. of the sample, with 150 c.c. of water, are shaken vigorously in a separator for 4 or 5 minutes, allowed to stand, and the aqueous layer drawn off into a separator of about 800 c.c. capacity. The remaining oily layer is again shaken with two successive quantities of 150 c.c. of water, and the two aqueous extracts added to the first. The whole is then saturated with common salt, and extracted twice with light petroleum, using 100 c.c. of the latter each time, and shaking vigorously.

The spirituous salt solution is separated and distilled till 75 c.c. are over, when the density of the distillate is taken and its reading at 60°F. in the Zeiss immersion refractometer observed. The difference between the observed refractometer reading and that of dilute ethyl alcohol of the same density as the distillate, is multiplied by a factor (which at the 15 p.c. limit may be taken as *unity*), and deducted from the percentage of proof spirit corresponding with the density of the distillate.

N.B.—The reason for this deduction is that owing to the presence in the distillate of a certain amount of the higher homologues of ethyl alcohol not eliminated by the treatment above described, the refractometer reading is higher than that of dilute ethyl alcohol of the same density, and indicates a higher percentage of proof spirit. The difference varies with the nature of the fusel oil and the percentage of ethyl alcohol present, and it has been found by experiment that the necessary deduction to be made from the apparent percentage of proof spirit, as deduced from the density of the distillate, is equivalent to the refraction difference multiplied by a factor which is greater than unity for percentages under 15, and less than unity when the percentage of proof spirit exceeds 15 p.c.

The mean factors obtained from an average fusel oil containing known percentages of dilute ethyl alcohol, equivalent to from 5–25 p.c. of proof spirit, vary from 1·4 to 0·8, the mean factor at the 15 p.c. limit imposed by the Revenue authorities being approximately unity. As the mean refractometer differences observed in distillates within the above limits (5 p.c. and 25 p.c.) do not differ greatly from 5 p.c., it follows that a distillate having an apparent strength of 20 p.c. proof spirit would have a real strength of 15 p.c. proof spirit.

Speaking generally, the real strength (expressed as a percentage of proof spirit) may be found by the formula

$$x = a - rf,$$

where a is the apparent percentage of proof spirit corresponding with the density of the distillate; r, the difference in the refractometer readings of the distillate and dilute ethyl alcohol of the same density; f, the factor to be employed; and x, the required percentage of proof spirit due to ethyl alcohol only. The different values of f may be found from observations made upon mixtures of fusel oil with various known proportions of ethyl alcohol.

The accurate estimation of fusel oil in spirit is extremely difficult. A very rapid and simple process introduced by Traube is said to give satisfactory results where great accuracy is not required. The specific gravity of the spirit having been determined, sufficient water is added to reduce the proportion of alcohol to 20 p.c. The liquor is sucked up and allowed to fall a few times in a carefully dried, thin-sided capillary tube, 20 cm. long, and about 0·8 mm. in diameter, fastened to a graduated scale, and terminating at the zero in two points, which are set by a stand moved upon screws, to the surface of the liquid in the vessel into which the capillary tube dips. The height to which the liquid rises decreases with a rise in the proportion of fusel oil. From the observed height of the liquid in the capillary tube (temperature 21°), the percentage of fusel oil may be ascertained from the following table (Girard and Cuniasse, l'Analyse des Alcools):—

Height in tube	P.c. of fusel oil	Height in tube	P.c. of fusel oil
53·6 mm.	0·0	48·85 mm.	0·6
52·7 ,,	0·1	48·20 ,,	0·7
51·85 ,,	0·2	47·45 ,,	0·8
51·0 ,,	0·3	46·75 ,,	0·9
50·3 ,,	0·4	46·15 ,,	1·0
49·6 ,,	0·5		

This process is said to be largely affected by accidental conditions, such as temperature, moisture in the tube, &c., and by the presence of nitrobenzene, oils of peppermint, fennel, orange, and carraway, amyl acetate, &c.

Further information on this process is given in Traube (Bied. Zentr. 15, 559; Ber. 19, 892; Chem. News, 53, 302; Rep. Anal. Chem. 6, 659); Stutzer and Reitmair (*ibid.* 6, 606); Dingl. poly. J. 268, 126; and Girard and Cuniasse.

An improved apparatus, which he calls a *stalagmometer*, has been introduced by Traube (Ber. 20, 2644) for this estimation. The liquid, diluted as above to 20 p.c., is filled to a mark in a vessel, and is allowed to fall drop by drop through a capillary tube at the base of the vessel, the number of drops in a certain time being noted and compared with the number of drops of pure alcohol of the same strength falling in the same time from the same apparatus. A smaller proportion of fusel oil than 0·05 p.c. may thus be determined.

The following table serves to indicate the percentage of fusel oil corresponding with the number of drops observed, (Girard and Cuniasse):—

Number of drops	P.c. of fusel oil	Number of drops	P.c. of fusel oil
100	0·0	108·5	0·6
101·8	0·1	109·9	0·7
103·6	0·2	111·5	0·8
105·0	0·3	113·1	0·9
106·3	0·4	114·7	1·0
107·5	0·5		

If the temperature of the spirit is higher or lower than that for which the instrument has been calibrated, the number of drops observed is increased or diminished by 0·1 drop for every 30 drops for each degree of difference.

Another process, first introduced by Röse (Pharm. Centr. 1886, 9), depends on the alteration produced by the presence of fusel oils in the solubility of 50 p.c. alcohol in chloroform, and is said to be scarcely affected by the bodies which influence the results obtained by Traube's method. This process, which is official in Germany and Switzerland, has been modified at various times by Stutzer, Reitmair, Herzfeld, Windisch, and others (*vide* Zeitsch. anal. Chem. 34, 1895). Bromwell's modification of Röse's fusel-oil apparatus (*v.* U.S. Dept. Agric. Bur. of Chem. Bul. 46, 59) consists of a pear-shaped bulb holding about 200 c.c., stoppered at the upper end, and having at the lower end a graduated stem of about 4 mm. internal diameter leading to another bulb of about 20 c.c. capacity, and terminating in a tube provided with a stop-cock. The narrow stem is graduated in 0·02 c.c. from 20·0 to 22·5 c.c.

Fusel-free alcohol is first prepared by fractional distillation over caustic alkali to resinise aldehydes, saponify esters, and saturate acids, and is diluted to exactly 30 p.c. by volume (sp.gr. 0·965 at 15·6°); a quantity of chloroform is dehydrated and redistilled, and a solution of sulphuric acid, of sp.gr. 1·2857 at 15·6° is prepared.

Of the sample under examination, 200 c.c are taken, made alkaline, and distilled until about 175 c.c. are over. After cooling, 25 c.c. of water are added to the distilling flask, and the distillation resumed until 200 c.c. are collected. The distillate is diluted to exactly 30 p.c. by volume (sp.gr. 0·965 at 15·6°) and this, together with the Röse apparatus and the flasks containing the reagents (fusel-free alcohol, chloroform, and sulphuric acid) is placed in a water-bath kept exactly at 15° until all have acquired a uniform temperature.

The apparatus is then filled to the 20 c.c. mark with chloroform (through the lower tube by suction), and 100 c.c. of the fusel-free alcohol and 1 c.c. of sulphuric acid added. The apparatus is inverted and shaken vigorously for 2 or 3 minutes, the stop-cock being momentarily opened once or twice to equalise pressure. The apparatus is then allowed to stand for 10 or 15 minutes in the water-bath at 15°, with occasional turning to hasten the separation of the reagents, and the volume of the chloroform is noted.

The apparatus is then thoroughly cleaned and dried, and the operation repeated, using the distillate from the sample instead of the fusel-free alcohol. An increase in the volume of the chloroform is observed due to the fusel oil present, and this difference, multiplied by the factor 0·663, gives the volume of fusel oil in 100 c.c., or the percentage of fusel oil by volume in the 30 p.c. distillate. This is then calculated to the percentage of fusel oil by volume in the original sample according to the alcoholic strength of the latter.

For example, in a sample containing 50 p.c. of alcohol by volume, the increase in the chloroform volume with the distillate from the sample diluted to 30 p.c. being 1·62 c.c., and that in the fusel-free alcohol also at 30 p.c. 1·42 cc., the difference is 0·20 c.c. The volume of fusel oil in 100 c.c. of the 30 p.c. distillate is, therefore, $0{\cdot}20 \times 0{\cdot}663 = 0{\cdot}1326$ c.c., and the percentage of fusel oil by volume in the sample (50 p.c. alcohol by volume) is $0{\cdot}1326 \times 50 \div 30 = 0{\cdot}221$.

In France, the official method is that of *Savalle* as modified by Girard and Cuniasse, and is based upon the depth of colour obtained by the action of strong sulphuric acid upon the higher alcohols. The method, which at best gives only comparative results, and these only when conducted under conditions so strict as to be almost unattainable in practice, is as follows:—

50 c.c. of the brandy, after distilling to free from colouring and extractive matters, and adjusted to contain 50 p.c. of absolute alcohol, are placed in a flask of about 250 c.c. capacity, and 1 gram of metaphenylenediamine is added, together with a little pumice.

The flask is adjusted to a reflux condenser and the contents boiled gently for an hour and then allowed to cool. The contents of the flask are then distilled to near dryness, and the distillate made up to the original volume of 50 c.c. with a few drops of distilled water. 10 c.c. of the spirit thus prepared are placed in a thoroughly clean flask of about 75 c.c. capacity, and 10 c.c. of pure concentrated sulphuric acid

are carefully run into the flask so that it forms a layer under the spirit. The contents of the flask are quickly mixed and heated over a Bunsen flame, with constant agitation for 15 seconds after the commencement of ebullition. The liquid set aside to cool, the mouth of the flask being covered with a small watch-glass. One or more samples of standard alcohol of 50 p.c. strength, and containing known quantities of *isobutyl* alcohol (50 mg. or less per 100 c.c.) are treated in exactly the same way. When cold, the colouration given by the sample under examination is compared with those given by the standard samples.

Beckmann's method depends upon the separation of the higher alcohols from the spirit by means of calcium chloride and carbon tetrachloride, the conversion of the higher alcohols into their nitrites by the action of sodium nitrite and sodium bisulphite, removing the excess of nitrous acid with sodium bicarbonate, decomposing the nitrites with sulphuric acid, and final titration of the nitrous acid thus obtained with permanganate.

The details of this process are as follows :—

25 to 50 c.c. of the spirit, after distillation to free it from any colouring or extractive matter, are taken and diluted with water, so that the mixture shall contain not more than 20–25 p.c. of absolute alcohol. The solution is then saturated with sodium or calcium chloride, and extracted four times successively by vigorously shaking with 40 c.c., 25 c.c., 25 c.c., and 10 c.c. of carbon tetrachloride. The carbon tetrachloride extracts are mixed, and then washed three times successively by shaking with 50 c.c., 25 c.c., and 25 c.c. of saturated salt solution, and once with 25 c.c. of saturated sodium sulphate solution. The washings of each are extracted with 25 c.c. of fresh carbon tetrachloride, and this after separation is added to the first carbon tetrachloride extract. The mixed carbon tetrachloride solution is then dried by shaking vigorously with freshly heated calcium chloride in powder.

To the dried tetrachloride solution 3 grams sodium nitrite and 3 grams of sodium bisulphite are added, and the mixture is shaken occasionally during an hour. It is then filtered through glass wool, and to the filtrate 3 grams of sodium bicarbonate are added, and the mixture shaken occasionally during half an hour. Then 20 c.c. of water are added, and the whole gently shaken and allowed to stand till the mixture separates into two layers. The separated carbon tetrachloride is then run off. To the remainder 10 c.c. of pure concentrated sulphuric acid are added; and, after shaking gently to mix, the mixture is poured into 100 c.c. of ice-cold water. The solution thus formed is titrated with standard permanganate (1 in 1000) until the pink colour becomes permanent. (The end reaction is not very sharp.)

(1 c.c. permanganate solution = 0·00278 grams amyl alcohol.)

According to Schidrowitz (*v. infra*), this method, as published, is unreliable, owing chiefly to the extraction of ethyl alcohol by the carbon tetrachloride.

The best method hitherto suggested is that of Marquardt, as modified by Allen and Schidrowitz. It is based upon the oxidation of the higher alcohols into the corresponding acids, and the estimation of the latter by titration or by converting them into and weighing their barium salts.

The extraction is carried out as in the Beckmann process just described. To the washed carbon tetrachloride solution 5 grams of pure powdered potassium dichromate, 2 c.c. of concentrated sulphuric acid, and 10 c.c. of water are added. The mixture is shaken and gently boiled for 8 hours under a reflux condenser. It is cooled, a little pumice and 50 c.c. of recently boiled distilled water are added, and it is then distilled to near dryness. The residue is cooled, 50 c.c. water added, and again distilled.

The distillates are mixed and titrated with N/10-baryta solution, first with methyl orange as indicator, and then with phenolphthalein. The acid indicated by the methyl orange is regarded as 'mineral acid,' and the difference as organic acid, which is calculated into amyl alcohol by multiplying the number of c.c. of N/10-baryta solution by 0·0088, and the figure indicating the dilution of the alcohol.

To obtain the combining weight, the solution containing the barium salt of the acid is separated from the carbon tetrachloride, evaporated, filtered, and finally dried in a platinum capsule and weighed. The weighed residue is then treated with a slight excess of sulphuric acid, again evaporated, and the barium sulphate ignited and weighed. From the weights found the combining weight of the acid is calculated.

By this method also some ethyl alcohol is extracted by the carbon tetrachloride, but apparently it does not appear as acetic acid after oxidation, and, according to Schidrowitz, the effect attributed to 'mineral acid' (of the presence of which there is no proof) may be due to some action between the methyl orange and certain aliphatic acids present.

(For a detailed criticism of the last three methods described, *see* Schidrowitz and Kaye, Analyst, June, 1905, and June, 1906.) J. C.

FUSTIC, YOUNG, *v.* YOUNG FUSTIC.

FUSTIN *v.* GLUCOSIDES; also YOUNG FUSTIC.

FUSTIN TANNATE *v.* YOUNG FUSTIC.

G

GADININE *v.* PTOMAÏNES.

GADOLINITE. A rare mineral consisting of silicate of yttrium earths, glucina, and ferrous oxide $Gl_2FeY_2Si_2O_{10}$. Analyses show about 40–45 p.c. of yttrium earths of molecular weight 250–290; the amount of erbia has been separately determined as 10–15 p.c. It occurs in much larger masses than the other rare-earth minerals, forming rough, black, and opaque crystals, sometimes exceeding 20 kilogs. in weight.

The crystals are monoclinic with an orthorhombic aspect; but in thin sections the material is optically isotropic. When heated, the mineral suddenly glows brightly, a molecular transformation taking place; the material then becomes optically birefringent, increases in sp.gr. (from 4·1–4·4 to 4·3–4·7), and changes in colour (as seen in sections) from greenish to reddish. Gadolinite occurs in some abundance as masses of considerable size in pegmatite veins at a few localities; notably, at Ytterby and near Falun in Sweden; in the felspar quarries of Sætersdalen and Hitterö, and elsewhere in the south-east of Norway; in Llano Co., Texas, and in Mohave Co., Arizona. The locality (Barringer Hill, five miles south of Bluffton) in Llano Co. has yielded masses of gadolinite weighing 200 lbs., in association with several other rare-earth minerals. These have been worked for the supply of yttrium and erbium earths used in the 'glower' of the Nernst lamp (W. E. Hidden, Amer. J. Sci. 1889, 38, 474; 1905, 19, 425). L. J. S.

GADOLINIUM. Gd = 157·3 (*cf.* Urbain, Compt. rend. 1905, 140, 583). This element was first identified by Marignac in 1880, who separated its salts from those of other rare-earth metals present in samarskite by fractional precipitation with potassium sulphate (Arch. de Genève, 1880, [3] 3, 413; Compt. rend. 1880, 90, 899). With europium and terbium, gadolinium forms the small group of terbium metals, and as the solubilities of its salts are intermediate between those of the other two members of the family, the final separation of gadolinium from these elements is a matter of considerable difficulty. The older methods of separation, precipitation by ammonia, crystallisation of the oxalates, formates, and double sulphates, or combinations of these processes, did not, in all probability, lead to the complete purification of gadolinium. The presence of small quantities of terbium is indicated by a faint yellow discolouration of the colourless gadolinia. Europium is indicated spectroscopically in the arc spectrum.

Sources. The crude yttrium earths from monazite sand, samarskite, ytterbite (gadolinite), xenotime, æschynite, &c.

Extraction and separation of the terbium earths. The first four methods outlined below serve rather to concentrate the terbium earths than to separate them from one another, gadolinium being the only one of the three which is obtained by these processes in a moderately pure condition.

A convenient starting-point for the separation of the terbium earths is the most soluble fraction of the ammonium or magnesium double nitrate separation of the rare earths. The preliminary elimination of the cerite metals with sodium or potassium sulphate is less preferable, since it involves a co-precipitation of a portion of the terbium group.

1. *Fractional precipitation with ammonia.*—In this process, terbia accumulates in the first fractions, followed successively by samaria and gadolinia. Accordingly, samaria is a weaker base than gadolinia, and this relationship forms an exception to the rule that the more electro-positive earths yield less soluble double sulphates and nitrates than the less electro-positive oxides (*cf.* Lecoq de Boisbaudran, Compt. rend. 1890, 111, 394; Bettendorf, Annalen, 1892, 270, 376; Benedicks, Zeitsch. anorg. Chem. 1900, 22, 393).

2. *Fractional crystallisation of the sodium and potassium double sulphates.*—In isolating gadolinia from samarskite, Marignac (*l.c.*) separated the less basic constituents of the yttrium earths by partially decomposing the nitrates, dissolved the oxides, consisting chiefly of yttria, samaria, and the terbium earths in nitric or hydrochloric acid, and precipitated fractionally with potassium sulphate solution. After a systematic course of fractionation, he obtained the following four fractions in descending order of solubility: (i.) yttrium, terbium; (ii.) gadolinium, purified by further fractionations with potassium sulphate; (iii.) samarium, didymium; (iv.) didymium (*cf.* Delafontaine, Arch. de Genève, 1878, 61, 273; Ann. Chim. Phys. 1878, [5] 14, 238; Lecoq de Boisbaudran, Compt. rend. 1883, 97, 1463; Bettendorf, *l.c.*).

3. *Fractional crystallisation of formates and oxalates.*—The sparing solubility of the formates of the terbium group has been utilised in the separation of these metals, these salts separating as white microcrystalline powders from the concentrated solutions (*cf.* Delafontaine, *l.c.*; Marignac, *l.c.*; Hofmann and Krüss, Zeitsch. anorg. Chem. 1893, 4, 27; Feit, *ibid.* 1905, 43, 267).

The terbium earths can also be separated from erbium and yttrium by precipitation with oxalic acid in nitric acid solution (Marignac and Delafontaine, *l.c.*).

4. *Fractional crystallisation of the ethyl sulphates.*—The systematic crystallisation of the ethyl sulphates of the rare earths from water or alcohol leads to a separation of the three principal groups; cerite earths, terbium earths, and yttrium earths, arranged in descending order of solubility (Urbain, Ann. Chim. Phys. 1900, [7] 19, 184).

5. *Fractional crystallisation of the nitrates.*—The more complete separation of the constituents of the terbium group has been accomplished by the use of the nitrates and double nitrates. By fractionating the nitrates of terbium earths containing samaria, the sparingly soluble gadolinium nitrate and the more readily soluble samarium nitrate were separated as well as a middle fraction rich in europium. The solubility of the rare-earth nitrates falls from lanthanum to samarium, attaining a minimum at gadolinium, and rises again till it reaches ytterbium.

By a lengthy fractionation of the nitrates from nitric acid (sp.gr. 1·3), Demarçay isolated small quantities of europium and gadolinium in a highly purified condition (Compt. rend. 1900, 130, 1469; 131, 343; 1901, 132, 1484). A further improvement in the separation was effected by Urbain and Lacombe (*v.* EUROPIUM), who crystallised the double magnesium nitrates of the rare earths in the presence of magnesium bismuth nitrate.

After crystallisation of the samarium and bismuth double salts, the mother liquor contains europium and gadolinium, the former being the first to separate on further fractionation. The gadolinium is then separated from the other remaining earths by fractionating the simple

nitrates in the presence of bismuth nitrate. The latter salt now causes a separation to occur between gadolinium and dysprosium, the middle fraction consisting of bismuth and terbium nitrates. In this way, gadolinium is completely freed from terbium, dysprosium, and erbium earths. The fractional crystallisation of the nickel double nitrates of the terbium earths has led to a similar separation (*cf.* Compt. rend, 1903, 137, 568, 792; 1904, 138, 84, 627; 139, 736; 1905, 140, 1233; 141, 521).

Compounds. The oxide and chloride of gadolinium are colourless; the solutions of the latter have no selective absorption in the visible region of the spectrum, but show four strong bands in the ultra-violet end. (For spark-spectrum, *v.* Compt. rend. 1890, 111, 472; 1896, 122, 728; 1900, 131, 343; 1905, 140, 1233; 141, 521, 954; Ber. 1901, 34, 2460; Annalen, 1891, 263, 164. For arc-spectrum, *v.* Eberhard, Zeitsch. anorg. Chem. 1905, 45, 394; Exner and Haschek, Die Wellenlängen der Bogenspektra, 1904.)

Gadolinia (*Gadolinium oxide*) Gd_2O_3, a white amorphous hygroscopic powder, absorbing carbon dioxide from the air; sp.gr. 7·407 at 15°.

Gadolinium chloride and **bromide** $GdCl_3,6H_2O$ and $GdBr_3,6H_2O$, soluble deliquescent salts, the former yielding the yellow double chlorides, $GdCl_3{\cdot}PtCl_4,10H_2O$, and $GdCl_3{\cdot}AuCl_3,10H_2O$.

Gadolinium fluoride GdF_3, a white gelatinous precipitate becoming granular on heating on the water-bath; somewhat soluble in hot hydrofluoric acid.

Gadolinium platinocyanide

$$2Gd(CN)_3{\cdot}Pt(CN)_2,18H_2O;$$

separates in red rhombic crystals with a green reflex; it resembles the isomorphous platinocyanides of yttrium and erbium, and differs from the corresponding double salts of the cerium group, which are yellow with a blue reflex.

Gadolinium nitrate $Gd(NO_3)_3,6H_2O$ or $5H_2O$, m.p. 91°–92°, is of all the nitrates of the rare earths the least soluble in nitric acid (*cf.* Demarçay, Compt. rend. 1900, 131, 343; *v.* Lang and Haitinger, Annalen, 1907, 351, 450). The following double nitrates:

$$2Gd(NO_3)_3{\cdot}3Mg(NO_3)_2,24H_2O$$

and $2Gd(NO_3)_3{\cdot}3Ni(NO_3)_2,24H_2O$, have been utilised in the isolation of gadolinium; the former melts at 77°.

Gadolinium sulphate $Gd_2(SO_4)_3,8H_2O$ separates from hot solutions in monoclinic crystals, isomorphous with yttrium sulphate.

Gadolinium sulphide Gd_2S_3, a yellow hygroscopic mass, sp.gr. 3·8, is produced by heating the sulphate in hydrogen sulphide; it is slowly decomposed by water.

Gadolinium acetate $Gd(H_3C_2O_2)_3,4H_2O$ forms moderately soluble triclinic crystals; the **Oxalate** $Gd_2(C_2O_4)_3,10H_2O$ separates from nitric acid solution in monoclinic crystals (*v.* Brauner, Chem. Soc. Trans. 1898, 73, 951); the **Malonate** $Gd_2(H_2C_3O_4)_3,8H_2O$ is obtained in refractive yellow needles (*v.* Erdmann and Wirth, Annalen, 1908, 361, 190). G. T. M.

GAHNITE, *Zinc aluminate* (*v.* ZINC).

GALACTIN *v.* GUMS.

GALACTOSE *v.* CARBOHYDRATES.

GALAFATITE. An aluminium potassium sulphate, named after the discoverer, found, amongst other places in Spain, at Benahabux near Almeria, where it occurs in parallel veins from 5 to 6 mm. thick. It is white when pure, has a sp.gr. 2·75, and hardness 3·5. It is treated by calcination, followed by lixiviation with water, whereby a solution of potassium sulphate and a residue of nearly pure alumina are obtained. The calcined ore contains 65–70 p.c. of alumina and 25–30 p.c. of potassium sulphate (Preuss, Eng. and Min. J. 1911, 91, 261; J. Soc. Chem. Ind. 1911, 30, 282).

GALALITH. Artificial horn prepared by the action of formaldehyde on casein. Skim milk is treated with caustic alkali or alkali carbonate, the casein is precipitated by the action of acid, pressed, impregnated with formaldehyde and dried (J. Soc. Chem. Ind. 1909, 101).

GALANGA ROOT. Galanga root is the rhizome of *Alpinia officinarum* (Hance.), and is a native of China.

Galanga root was first examined by Brandes (Arch. Pharm. [2] 19, 52), who isolated from it a substance which he named *kæmpferide*, but this, according to Jahns (Ber. 1881, 14, 2385), was a mixture of three substances, *kæmpferide*, *alpinin*, and *galangin*. The subject was later examined by Gordin (Dissert, Berne, 1897), and by Ciamician and Silber (Ber. 1899, 32, 861) and Testoni (Gazz. chim. ital. 1900, 30, ii. 327), and it is now clearly demonstrated that galanga root contains *kæmpferide*, *galangin*, and *galangin monomethylether*. According to Testoni, the alpinin of Jahns is a mixture of galangin and kæmpferide.

Kæmpferide $C_{16}H_{12}O_6$ consists of yellow needles, m.p. 227°–229°, soluble in alkaline solutions with a yellow colour. Sulphuric acid gives a blue fluorescent yellow solution.

Triacetylkæmpferide $C_{16}H_9O_6(C_2H_3O)_3$, colourless needles, m.p. 193°–194° (C. & S. and T.) (compare also Jahns), *tribenzoylkæmpferide* $C_{16}H_9O_6(C_7H_5O)_3$, m.p. 177°–178° (T.), *kæmpferide diethylether* $C_{16}H_{10}O_6(OC_2H_5)_2$ (T.), yellow needles, m.p. 137°–139°, and *dibromkæmpferide* $C_{16}H_{10}Br_2O_6$, yellow needles, m.p. 224°–225° (decomp.) (J.) have been prepared. In the presence of acetic acid, kæmpferide yields, by means of mineral acids, yellow crystalline compounds, and alcoholic potassium acetate gives *monopotassium kæmpferide*

$$C_{16}H_{11}O_6K,H_2O,$$

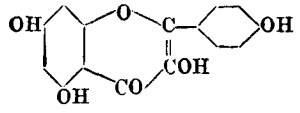
yellow needles, which are decomposed by boiling water (Perkin and Wilson, Chem. Soc. Trans. 1903, 83, 136). Kæmpferide is in reality *kæmpferol monomethylether* (v. Kostanecki and Rozycki, Ber. 1891, 24, 3723).

Kæmpferol $C_{15}H_{10}O_6$ is produced when kæmpferide is digested with strong hydriodic acid, and consists of yellow needles, m.p. 271° (K. & R.), 276°–277° (Perkin), soluble in alkaline solutions with a yellow colour.

Tetra-acetylkæmpferol $C_{15}H_6O_6(C_2H_3O)_4$, when crystallised from methyl alcohol, forms colourless needles, and when heated begins to melt at 116°, and becomes completely fluid at 120°. On further heating, however, gradual solidification ensues, and the product subsequently melts at 181°–182° (Perkin and Wilkinson, Chem. Soc. Trans. 1902, 81, 587). *Tribromkæmpferol* $C_{15}H_7Br_3O_6$ forms yellow needles, m.p. 275°–277°, *kæmpferol sulphate*

$C_{15}H_{10}O_6,H_2SO_4$, orange-red needles; *kæmpferol hydriodide* $C_{15}H_{10}O_6,HI$ needles, and *monopotassium kæmpferol* $C_{15}H_9O_6K$, *orange-yellow prismatic needles* (P. & W.). Fused with alkali, kæmpferol gives *phloroglucinol* and *p-hydroxybenzoic acid*.

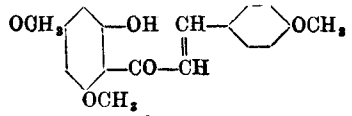
To kæmpferol, v. Kostanecki assigned the constitution of a *trihydroxyflavonol* (Ber. 1901, 34, 3723).



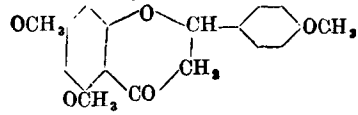
and this compound has been synthesised by v. Kostanecki and Tambor (Ber. 1904, 37, 792).

2-*Hydroxy*-4′ : 6′ : 4-*trimethoxychalkone* (1), when digested with boiling dilute alcoholic sulphuric acid, gives 1 : 3 : 4′-*trimethoxyflavanone* (2)

(1)

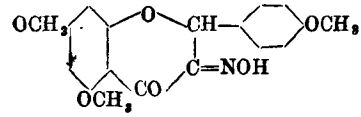


(2)

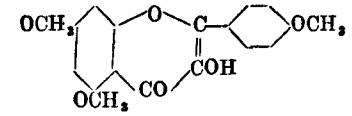


and the latter, by means of amyl nitrite and hydrochloric acid, is converted into *iso*nitroso-1:3:4′-trimethoxyflavanone (3). When a solution of this substance in acetic acid is boiled with 10 p.c. sulphuric acid, 1:3:4′-trimethoxyflavonol is produced (4), from which, by the action of hydriodic acid, kæmpferol is readily prepared (5).

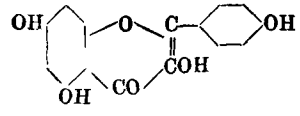
(3)



(4)



(5)

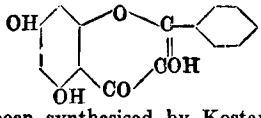


Kæmpferol possesses well-defined dyeing properties, and gives with mordanted woollen cloth the following shades (P. & W.):—

Chromium.	*Aluminium.*	*Tin.*	*Iron.*
Brownish-yellow.	Yellow.	Lemon-yellow.	Deep olive brown.

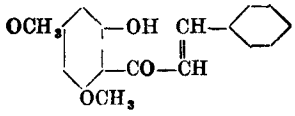
Galangin $C_{15}H_{10}O_5$, the second constituent of galanga root, crystallises in yellowish-white needles, m.p. 214°-215°, soluble in alkaline solutions with a yellow colour. With acetic anhydride, it gives a *triacetyl* derivative $C_{15}H_7O_5(C_2H_3O)_3$, m.p. 140°-142° (Jahns), and by means of methyl iodide, a dimethylether $C_{15}H_8O_5(OCH_3)_2$, m.p. 142°, is formed.

Galangin gives crystalline compounds with mineral acids in the presence of acetic acid, and reacts with alcoholic potassium acetate, yielding *monopotassium galangin*, yellow needles (P. & W.). When fused with alkali, *phloroglucinol* and *benzoic acid* are obtained. Galangin is a *trihydroxyflavonol*



and has been synthesised by Kostanecki and Tambor (Ber. 1899, 32, 2260), by a similar series of reactions to those employed in the preparation of kæmpferol.

2-Hydroxy-4′:6′-dimethoxychalkone

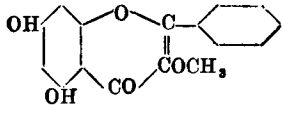


was converted into the corresponding flavanone, and the latter into its *iso*nitrosoderivative. This compound, on boiling with dilute sulphuric acid, gave 1:3-dimethoxyflavonol which, when heated with hydriodic acid, was transformed into galangin. Galangin gives, with mordanted woollen cloth, the following shades:—

Chromium.	*Aluminium.*	*Tin.*	*Iron.*
Olive-yellow.	Yellow.	Lemon-yellow.	Deep olive.

Galangin monomethylether $C_{15}H_9O_4(OCH_3)$ was first isolated from galanga root by Testoni (*l.c.*). It crystallises from methyl alcohol in bright-yellow prisms, melts at about 300°, and dissolves in strong alkaline solutions with a yellow colour. *Diacetylgalangin monomethylether* $C_{16}H_{10}O_5(C_2H_3O)_2$ forms yellowish-white leaflets, melting at 175°-176°.

When air is aspirated through an alkaline solution of galingin monomethyl ether, it is oxidised with formation of *benzoic acid* and *phloroglucinol* (Perkin and Allison), and therefore possesses the constitution :—



Other Sources of Kæmpferol.

Kæmpferol has been isolated from the blue flowers of the *Delphinium Consolida* (L.) (Perkin and Wilkinson, Chem. Soc. Trans. 1902, 81, 586), and in addition to quercetin from the flowers of the *Prunus spinosa* (L.) (Perkin and Phipps, *ibid.* 1904, 85, 56). Two glucosides of this colouring matter, known as *robinin* and *kæmpferitrin*, have also been shown respectively to exist in the flowers of the *Robinia Pseud-acacia* (L.) and the leaves of the *Indigofera arrecta* (Hochst.).

Robinin was first isolated from the flowers of the *R. Pseud-acacia* by Zwenger and Dronke (Annalen, Suppl. 1861, 1, 263), who considered that it was a glucoside of quercetin. Perkin (Chem. Soc. Trans. 1902, 81, 473) has shown that this is not the case.

To prepare the glucoside, the flowers are

exhausted with boiling alcohol, the solution concentrated by evaporation, and poured into water. The mixture is extracted with ether, and the aqueous liquid distilled down to a small bulk. On standing, crystals of robinin separate, which are purified by crystallisation from water.

Robinin consists of pale yellow needles, sintering at 190° and melting at 196°–197°, and when air-dried it possesses the formula

$$C_{33}H_{42}O_{20},8H_2O.$$

Boiling dilute sulphuric acid hydrolyses robinin with formation of *kæmpferol*, two molecules of *rhamnose* and one of *glucose*, according to the following equation:—

$$C_{33}H_{42}O_{20}+4H_2O = C_{15}H_{10}O_6+2C_6H_{14}O_6+C_6H_{12}O_6.$$

It is consequently a most interesting glucoside, as it appears to be the first known substance of this class which yields three sugar nuclei.

Kæmpferitrin (Perkin, Chem. Soc. Trans. 1907, 91, 437) $C_{27}H_{30}O_{14},3\frac{1}{2}H_2O$ is hydrolysed by acids with production of kæmpferol and two molecules of rhamnose. A description of this substance is given in the article on INDIGO, NATURAL. A. G. P.

GALBA *v.* RESINS.

GALBANUM *v.* GUM RESINS.

GALENA (Ger. *Bleiglanz*; Fr. *Galène*). Native lead sulphide (PbS), the principal ore of lead (86·6 p.c.). It crystallises in the cubic system, and possesses three directions of perfect cleavage parallel to the faces of the cube. Well-developed crystals, with the form of the cube or cubo-octahedron, are not uncommon. The massive mineral is always readily recognised by its rectangular stepped cleavages with smooth and brilliant surfaces and a lead-grey colour: small broken fragments have the form of cubes or dice. Further, it can be readily scratched with a knife (H=2½) yielding a black powder, and it is very heavy (sp.gr. 7·5). Ore with a very fine-grained texture may present somewhat the appearance of steel.

The presence of small quantities of silver in galena is of importance; though usually not more than a few ounces per ton in amount, it may reach 1 p.c. It is probably present in solid solution as silver sulphide, since argentite (*q.v.*) is isomorphous with galena. Examining polished surfaces of galena by reflected light under the high powers of a microscope, A. M. Finlayson (Quart. J. Geol. Soc. 1910, 66, 319) was able to detect fine strings of native silver running along the cleavage cracks of the galena. This was, however, only detected in specimens taken from the higher levels within reach of surface waters; specimens taken from deeper levels, where there has been no secondary alteration, showed no native silver.

Galena occurs chiefly in veins traversing rocks of various kinds, and also filling cavities in limestone. It is abundant in all lead-mining districts, and by its alteration it gives rise to cerussite, anglesite, and other secondary lead-bearing minerals. The use of galena for glazing pottery gave rise to the names 'potters' ore,' alquifoux (Fr.), and archifoglio (Ital.). L. J. S.

GALIPOT *v.* RESINS.

GALL-NUTS or GALLS or Oak Apples. (*Noix de Galle*, Fr.; *Gallen, Gallapfeln*, Ger.)

Galls are excrescences induced on plants by the attacks of animals (especially insects) or of other plants (especially fungi), which stimulate plant tissue that is capable of growing and cause this to hypertrophy. When an insect is the organism responsible, it usually infects very young parts (of roots, stems, or leaves), *in* which it deposits eggs from which there develop inside the gall larvæ and eventually mature insects.

The oak apples are thus caused by various species of gall wasps (*Cynipida*). The most important of these are those of north-temperate Europe and of the Levant. Of the former, one of the commonest on the common oak *Quercus sessiflora* (Salisb.) and *Q. pedunculata* (Ehrh.) is caused by *Cynips kollari*, and is like a yellowish-brown marble in size and shape, contains one central chamber, and eventually shows one little exit hole through which the insect has escaped.

More important are the Levant galls, induced on scrubby oaks belonging to the species *Q. lusitanica* (Lam.) [*Q. infectoria* (Oliver)], which occurs in the region extending from Greece, through Asia Minor, to Persia. The insect responsible is *Cynips tinctoria* (Htg.); this causes a gall by laying an egg in the young stem, which thereafter, by cell division and growth, swells into a gall in which the larva develops. The resultant insect may die inside the gall, or may bore its way out and escape through an exit hole. Levant galls are spherical to pear-shaped: the half near the stalk usually has a smooth surface, often inclined to be glossy, whereas the distal half is raised into lumps which are often conical in shape.

The Levant gall is very rich in tannin. Manceau found that the chemical composition in percentages was: water 12·05, ligneous substances 19·2, tannin 58·52, other constituents 10·21.

Levant galls vary in quality according to the region of origin, time of collection (including the condition as to whether gathered before or after the insects escape). The best kinds come from the Aleppo district: those gathered first, namely, in August or September, are of the highest quality, and are green, but subsequently become dark-coloured and harder: those gathered somewhat later are white, while the galls allowed to hang until winter are reddish-brown. Three qualities of Levant galls may be distinguished: (i.) Aleppo galls, small (2.5 cm. in diameter), dark-green to black in colour; (ii.) lighter-coloured galls, presenting the appearance of having been powdered on the surface; (iii.) Smyrna galls, larger (3–5 cm. in diameter), usually yellowish in tint. In water, the dark-hued galls sink, whereas the inferior lighter-tinted galls (even when dyed to imitate the former) float.

Galls (oak apples) of the same type are obtained in Southern Europe from scrubby specimens of *Quercus sessiliflora* (Salisb.) and *Q. pubescens* (Willd.).

GALLACETOPHENONE *v.* KETONES.

GALLAMINE BLUE, GALLANILIC BLUE, -VIOLET *v.* OXAZINE COLOURING MATTERS.

GALLEÏN. *Anthracene violet* (*v.* ALIZARIN AND ALLIED COLOURING MATTERS).

GALLIC ACID, 3:4:5-*Trihydroxybenzoic acid*

$C_6H_2(OH)_3COOH$, occurs in sumach, divi divi, Chinese tea, and various other plants (Stenhouse, Annalen, 45, 9; Hlasiwetz and Malin, Zeitsch. Chem. 1867, 271; Kawalier, J. 1852, 683; Perkin and Gunnell, Chem. Soc. Trans. 1896, 1307; Easterfield, *ibid.* 1901, 122; Grüttner, Arch. Pharm. 236, 293). Formed from tannin by boiling with dilute sulphuric acid, or when solutions of tannin become mouldy (Niernstein, Chem. Zeit. 33, 126; Ber. 1910, 628), or by heating tannin with zinc (Iljin, J. pr. Chem. 80, [2] 332). In order to prepare it, finely powdered *gall*-nuts are macerated for some days with cold water, and the decanted liquid is exposed to the air and allowed to become covered with mould. An addition of yeast is advantageous. The gallic acid, which separates, is purified by recrystallisation from boiling water (Wittstein, J. 1853, 435; Tieghem, Zeitsch. Chem. 1868, 222; Scheele and Steer, J. 1856, 482). Heinemann (Fr. Pat. 314863; J. Soc. Chem. Ind. 1902, 415) boils the aqueous extract of galls with 5 p.c. by weight of sulphuric acid for about 5 hours. The reaction is complete when a drop of the solution gives no precipitate with a gelatin solution (*v.* also Soc. Anon. Manuf. de Prod. Chimiques et Pharm. J. Soc. Chem. Ind. 1900, 553). It is soluble in 3 parts of boiling, in 130 parts of cold water; crystallises in silky needles or triclinic prisms from water with 1 mol. H_2O, which it loses at 120°; is most readily soluble in acetone (Rosenheim and Schidrowitz, Chem. Soc. Trans. 1898, 882); melts at 222°–240°; and when heated to a higher temperature decomposes into carbon dioxide and pyrogallol (Braconnot, Annalen, 1, 26; Pelouze, *ibid.* 10, 159; Liebig, *ibid.* 101; 47; de Luynes and Esperandiew, Zeitsch. Chem. 1, [2] 702; Thorpe, Pharm. J. 11, [3] 990). By heating equal weights of gallic acid and aniline, gallanilide is formed, which may be used as a germicide. It is non-toxic. When gallic acid is heated with twice its weight of aniline, and the aniline pyrogallate thus formed is boiled with benzene, pure pyrogallol is obtained (Cazeneuve, Bull. Soc. chim. 7, [3] 549; 11, 81, 82; Compt. rend. 117, 47). By the destructive distillation of ethyl gallate, pyrogallol, ethyl alcohol, and *rufigallic acid* (hexahydroxyanthraquinone) are produced (Perkin, Chem. Soc. Proc. 1902, 254). Rufigallic acid is also formed when gallic acid is heated with concentrated sulphuric acid (Robiquet, Annalen, 19, 204; Wagner, Chem. Zentr. 1861, 47; Löwe, J. pr. Chem. [i] 107, 296; Jaffé, Ber. 1870, 694; Klobukowski and Noelting, *ibid.* 1875, 819; 1876, 1256; 1877, 880; Widmann, *ibid.* 1876, 856), and on reduction with sodium amalgam yields *alizarin* (Widmann, *l.c.*; Bull. Soc. chim. 24, [2] 359). By heating a mixture of gallic and benzoic acids with sulphuric acid, *anthragallol* (trihydroxyanthraquinone) is produced (Seuberlich, Ber. 1877, 39).

Gallic acid, on oxidation with nitric acid, chlorine, or copper sulphate and alkali, yields oxalic acid as the main product (Boettinger, Annalen, 257, 248; 260, 337; Biétrix, Compt. rend. 122, 1545); oxidation with persulphates in the presence of acetic and sulphuric acids, yields *ellagic acid* (Perkin, Chem. Soc. Trans. 1905, 1412), and in the presence of dilute sulphuric acid, *flavellagic acid* (Perkin, *ibid.* 1906, 252); electrolytic oxidation with potassium ferricyanide in the presence of sodium acetate or other electrolytes, yields purpurogallincarboxylic acid (A. G. and F. M. Perkin, *ibid.* 1904, 254; 1908, 118; Perkin and Nierenstein, *ibid.* 1905, 1429); oxidation in alkaline solution yields *galloflavin*. Gallic acid is not reduced appreciably in acid or neutral solution, but in alkaline solution, benzoic acid is formed (Gardner and Hodgson, Chem. Soc. Proc. 1908, 272; Guignet, Compt. rend. 113, 200). Gallic acid and its derivatives undergo condensation with nitrosodialkylanilines to form dyestuffs of the *oxazine* or *gallo-cyanine group* (Patent Literature, Frdl. i. 267–270; ii. 158, 167–173; iv. 485, 506; *v.* also OXAZINE COLOURING MATTERS); with *o*-nitrosonaphthols or *o*-aminonaphthols to form brown dyestuffs used in tanning (Ashworth and Sandoz, D. R. P. 75633, 75634; Frdl. iv. 504, 505); with salicylic acid by means of phosphorus oxychloride to produce *salitannol*, an antiseptic used for dressing wounds (Bayer & Co., Eng. Pat. 9898; J. Soc. Chem. Ind. 1898, 487; Dœbner, D. R. P. 94281; Chem. Zentr. 1898, i. 229); with acetaldehyde and benzaldehyde, yielding compounds which become coloured when dissolved in acids (Kahl, Ber. 1898, 151); with acetic acid and acetic anhydride to yield mono- and di- acetyl derivatives of gallic anhydride. These substances are insoluble in alkali, and so can be used instead of tannin for medicinal purposes, as the latter is soluble in the stomach juices (Bayer & Co., Eng. Pat. 1228; J. Soc. Chem. Ind. 1895, 297). Gallic acid is also used in the preparation of *thionine* dyestuffs (Nietzki, D. R. P. 73556, 76923, 79172; Frdl. iii. 360; iv. 455, 456).

Gallic acid condenses with formaldehyde to yield four distinct methylenedigallic acids, yielding dyestuffs on treatment with nitrosulphuric acid in sulphuric acid solution (Möhlau and Kahl, Ber. 1898, 259). It forms compounds with albuminoids (Wörner, D. R. P. 189334; J. Soc. Chem. Ind. 1908, 644), and with ferments (D. R. P. 198305; J. Soc. Chem. Ind. 1908, 713). It is absorbed by organic colloids, this being of interest, since it bears on the theory of dyeing and tanning processes (Dreaper and Wilson, J. Soc. Chem. Ind. 1906, 515). Complex salts of gallic acid (*v.* Silbermann and Ozorovitz, Chem. Zentr. 1908, ii. 1024). Derivatives of gallic acid (*v.* Power and Shedden, Chem. Soc. Trans. 1902, 73).

Basic bismuth gallate (*Dermatol*)

$C_7H_3O_5Bi,2H_2O$

is prepared from bismuth hydroxide and gallic acid, or from bismuth nitrate and gallic acid in the presence of potassium nitrate and acetic acid. It is a yellow powder, but is obtained crystalline by the second method given above (Thibault, J. Pharm. 14, [vi.] 487; 25, [vii.] 268; May, Amer. J. Pharm. 80, 208; Causse, Compt. rend. 117, 232; Fischer and Grützner, Arch. Pharm. 231, 680). *Bismuthhydroxyiodogallate* (*Airol*) is a greenish-grey powder (Haegler, Chem. Zentr. 1896, i. 764; Torelli, *ibid.* 1898, i. 857; Hoffmann, Traub & Co. D. R. P. 80399, 82593; Frdl. iv. 1122, 1123). Both compounds are inodorous antiseptics, and may be used as substitutes for iodoform.

Methyl ester $(HO)_3C_6H_2{\cdot}CO_2CH_3$. Prepared

by dissolving gallic acid in hot methyl alcohol, and treating the solution with hydrogen chloride. The alcohol is distilled off, the residue dried and recrystallised from hot water (Kern, Eng. Pat. 5953; D. R. P. 45786; Frdl. ii. 167; Hamburg, Monatsh. 19, 594): m.p. (anhydrous from methyl alcohol) 202°; from hot water, crystals contain water of crystallisation, which is driven off at 100°–110°.

Detection and Estimation.—Gallic acid gives a bluish-black precipitate with ferric chloride, but does not precipitate gelatin. On adding 1 c.c. of (1 : 30) potassium cyanide solution to a 1 p.c. solution of gallic acid and agitating, a ruby-red colour is produced, which disappears on standing, but is regenerated by agitation. Pyrogallol and tannic acid give yellowish-red solutions (Griggi, Boll. Chim. Farm. 38, 5). Boettinger (Annalen, 256, 341; J. Soc. Chem. Ind. 1900, 450) heats gallic acid with double its weight of phenylhydrazine to 100°, boils the solution for a few seconds, and then lets one drop fall into a beaker containing water made alkaline with caustic soda, when an orange or golden-yellow colouration is produced. Tannic acid gives a blue colouration changing to yellow. In estimating gallic acid in tannins, it is always necessary to separate it from the tannic acid, which is also present (Spica, Gazz. chim. ital. 31, ii. 201; Harnack, Arch. Pharm. 234, 537; Buchner, Annalen, 53, 537; Hinsdale, Chem. News, 64, 51; Dreaper, J. Soc. Chem. Ind. 1893, 412; Chem. News, 90, 111; Procter and Bennett, J. Soc. Chem. Ind. 1906, 251; Jean, *ibid.* 1900, 382).

GALLIPEINE *v.* CUSPARIA BARK.

GALLISIN (iso-**MALTOSE**) *v.* CARBOHYDRATES.

GALLIUM. Ga. At.wt. 69·9 (Boisbaudran). Is very widely distributed in nature, although always occurring in minute quantities. It is found in various clay ironstones, in hæmatites, in various aluminous and manganese minerals and ores, in some meteorites and meteoric iron, in zincblendes, pyrites, etc. (Hartley and Ramage, Chem. Soc. Trans. 1897, 533). Perhaps the richest source of this metal is the Middlesborough blast furnace metal obtained from the Cleveland clay ironstone, the cast iron containing 1 part of gallium per 33,000 parts of iron. Gallium belongs to the aluminium group of elements; it is the eka-aluminium predicted by Mendeléeff, and was discovered by Boisbaudran in 1875, by means of spectroscopic analysis, in the zincblende of Pierrefitte in the Pyrenees (Compt. rend. 1892, 114, 815). A quantity of the element was prepared by Boisbaudran and Jungfleisch (Compt. rend. 1878, 86, 475).

Gallium is a bluish-white, hard, tough, slightly malleable metal: sp.gr. 5·9, sp.ht. 0·080 and of higher sp. resistance than the alkali metals. It fuses at 30·1°, forming a silver-white liquid, resolidifying very slowly even at 0°. If, however, a fragment of solid gallium is introduced, it solidifies rapidly in pyramidal monoclinic crystals. The molten metal, if poured on to a glass, covers the surface with a bright mirror-like deposit. The metal is non-volatile at a red heat, is slowly and superficially tarnished in air or water. It is attacked by the halogens, and dissolves in hydrochloric acid and in potash solution with evolution of hydrogen. In nitric acid, it dissolves on warming, with evolution of oxides of nitrogen.

Compounds. *Gallium oxide* Ga_2O_3 is a white powder reduced by hydrogen at a bright red heat, and, according to Winkler (Ber. 1890, 23, 788), also by magnesium: the *hydroxide* is insoluble in water, but soluble in alkalis. *Chlorides*, $GaCl_3$, $GaCl_2$, an *oxychloride*, *bromides*, *iodides*, *sulphates*, *sulphides*, a *nitrate*, an *alum* $Ga_2(SO_4)_3{\cdot}(NH_4)_2SO_4{,}24H_2O$, and a *silicotungstate* have been prepared (Dupré, Compt. rend. 1878, 86, 720; Boisbaudran, Ann. Chim. Phys. 1877, [5] 10, 126; Wyruboff, Bull. Soc. franc. Min. 1896, 19, 240).

GALLOCYANINE *v.* OXAZINE COLOURING MATTERS.

GALLOFLAVIN. This dye, which can be fixed on mordanted fibres like alizarin, is obtained by the action of air, *i.e.* oxygen, on alkaline solutions of gallic acid. The process of oxidation depends on the amount of alkali present. In practice, 5 parts of gallic acid are dissolved in 80 parts of alcohol of 96°Tw. and 100 parts of water. The cooled solution is gradually mixed with 17 parts of caustic potash solution of 30°B., stirring all the while, and never allowing the temperature to rise above 10°. It is then exposed to the action of oxygen, either by blowing air through it or by agitating it briskly. The progress of the oxidation shows itself by the liquor assuming at first an olive-green or greenish-brown colour, until finally a crystalline precipitate separates out. When the amount of this precipitate no longer increases, the operation is finished. The mass of crystals is quickly filtered, dissolved in warm water, decomposed with hydrochloric or sulphuric acid, and boiled when the dye is precipitated in the state of glistening greenish-yellow plates. These are washed, and can then be applied for dyeing or printing.

Galloflavin dyes cotton mordanted with alumina greenish-yellow, which turns into a very brilliant yellow by treatment with tin crystals. Wool, mordanted with bichrome, is dyed olive-yellow, copper as mordant gives a dark-brown, and stannous mordant dull-orange. In practice, only chrome mordants are used, and the shades obtained are fairly fast to light, soap, and milling, fast to dilute acids and alkalis, but do not compare favourably with the alizarins. The colour is somewhat sensitive to chlorine.

The formula $C_{13}H_8O_9$ was first suggested for galloflavin (Bohn and Graebe), and subsequently $C_{12}H_6O_8$ (Herzig). The substance crystallises in greenish-yellow leaflets, is sparingly soluble in water, alcohol, and ether, more readily soluble in glacial acetic acid and aniline. The *potassium salt* $C_{13}H_4O_9K_2$ (B. & G.) is a crystalline body which is insoluble in alcohol and cold water. The *acetyl derivative*

$$C_{13}H_4O_5(O{\cdot}COCH_3)_4$$

(B. & G.) or $C_{12}H_2O_4(O{\cdot}COCH_3)_4$ (H.) crystallises from benzene or ethyl acetate in white needles, m.p. 230° (B. & G.), 230°–233° (H.); is freely soluble in glacial acetic acid and chloroform, but does not dissolve readily in alcohol or ether. The *chloracetyl derivative* $C_{13}H_2O_5(O{\cdot}COCH_2Cl)_4$ (B. & G.), is very little soluble in alcohol, ether,

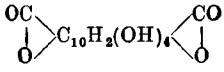
chloroform, or benzene, easily soluble in acetic acid, and crystallises in needles; m.p. 210°–212°. Galloflavin, on methylation, yields *tetramethoxygalloflavin* $C_{12}H_2O_4(OCH_3)_4$ (H.), crystallising in felted, almost colourless needles from acetic acid; m.p. 236°–239°. When this compound is quickly boiled with aqueous potash, and then treated with strong hydrochloric acid, it yields a crystalline substance, *trimethylisogalloflavin*, $C_{11}H_2O_3(OCH_3)_3COOH$ (H.), difficultly soluble in alcohol, and crystallising therefrom in fine white needles, melting at 253°–256°, with strong gas evolution. On methylation or esterification, this yields *tetramethylisogalloflavin*

$$C_{11}H_2O_3(OCH_3)_3COOCH_3$$

(H.), crystallising from alcohol in long needles; m.p. 232°–234°. Heated under reduced pressure, trimethyl*iso*galloflavin loses carbon dioxide, and *a substance*, $C_{11}H_3O_3(OCH_3)_3$ (H.), distils over at 270°–300° (28 mm. pressure), which sets to a yellowish-white crystalline mass, is difficultly soluble in alcohol, and can be crystallised therefrom in white crystals; m.p. 130°–134°. On methylating trimethyl*iso*galloflavin with aqueous alcoholic potash and methyl sulphate, and finally with diazomethane, there is obtained *a substance*, $C_{10}H_2O(OCH_3)_4(COOCH_3)_2$ (H.), crystallising out of methyl alcohol and melting at 92°–95°. This substance is easily hydrolysed to the corresponding *dibasic acid*

$$C_{10}H_2O(OCH_3)_4(COOH)_2$$

(H.), crystallising from dilute methyl alcohol, and melting at 214°–215° with gas evolution. This dibasic acid, on heating under reduced pressure, loses carbon dioxide, and *a monobasic acid* $C_{10}H_3O(OCH_3)_4COOH$ (H.) distils over at 260°–280° (28 mm. pressure), which sets to a solid, and, crystallised from ethyl acetate, melts at 132°–135°. This series of transformations from tetramethylgalloflavin indicates that it probably contains two lactone bonds, and that galloflavin itself may be represented as:



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GALLOGEN, GALLOL *v.* SYNTHETIC DRUGS.

GALLOTANNIC ACID *v. Digallic acid*, art. TANNINS.

GALVANISED IRON *v.* ZINC.

GAMBINE. *Nitroso-β-naphthol* (*v.* QUINONE-OXIME DYES).

GAMBIR or **GAMBIER.** The Malayan name of an extract obtained from the *Uncaria Gambier* (Roxb.). It is the *Terra japonica* of tanners (*see* CATECHU).

GAMBOGE *v.* GUM RESINS.

GAMMAM. A Tunisian dyestuff of unknown origin.

GANNISTER. The name of a bed of highly silicious fire-clay used for the lining of the Bessemer converter and for similar purposes. When crushed, and, if necessary, mixed with plastic clay, it produces a highly refractory fire brick.

GARANCEUX and **GARANCINE** *v.* MADDER.

GARBAGE FATS. Under the name 'garbage fats' may be comprised all those fats contained in house and other refuse which do not find their way into the sewers. Such refuse is generally collected by the municipalities and destroyed as soon as possible, the primary object being to remove it rapidly from inhabited areas and dispose of it in a sanitary, or at any rate in the least objectionable, manner. The system in vogue in this country, and rapidly superseding the older method of dumping on waste land, is to destroy the refuse in specially designed destructors, after a rough sorting out of tins, iron pots, old leather, &c., has taken place in the destructor works. Thus all putrescible matter, together with the fat present, is destroyed. Hence efforts have not been wanting to recover the fatty matter. In the United States of America especially methods for the disposal of garbage have been developed. An early process (worked in Buffalo about 1885) consisted in extracting the garbage with light petroleum. This has, however, been superseded by cheaper processes comprised under the term 'reduction processes.' These processes closely simulate the methods used in the rendering of fish oils (*see* MENHADEN OIL), and slaughter-house greases.

In several cities of America, the Arnold-Egerton process is worked, in which the fatty matter is extracted by purely mechanical means. The garbage is delivered into large digestors, in which the mass is boiled with steam. After boiling at 80 lbs. pressure, the whole mass collects into three layers, the top layer of which forms the separated grease. This grease is sold for the manufacture of low-class soaps and low-class lubricants. It has a dark-brown colour, and is characterised by a large amount of free fatty acids and unsponifiable matter. J. L.

GARCINIA INDICA (Choisy). A plant belonging to the order *Guttiferæ*. The pericarp of the fruit is used at Goa as a spice, and the blood-red acid juice as a lemonade. The seeds yield 30 p.c. of fat, which contains 50 p.c. of stearic acid. The cake left after the removal of the fat contains a fine red colouring matter soluble in water and alcohol (Bouis and Pimentel, Compt. rend. 44, 1355).

GARLIC. *Allium sativum* var. *vulgare* (Döll.). A plant extensively used as a condiment in Spain, Portugal, Northern Africa, and other countries.

König gives as its average composition—

Water	Protein	Fat	Carbohydrates	Fibre	Ash
64·6	6·8	0·1	26·3	0·8	1·4

Among the carbohydrates is included 0·9 p.c. of pentosans. The characteristic odour and flavour of garlic are due to an essential oil, amounting to about 0·2 p.c. of the weight, which consists mainly of sulphide and allyl *iso*thiocyanate, the former largely predominating. A wild species, *Allium vineale*, is a troublesome weed in pastures and meadows, and when eaten by dairy cows imparts its disagreeable flavour to the milk. H. I.

GARNET (Ger. *Granat*; Fr. *Grenat*). A group of minerals differing widely in chemical composition, but all conforming to the general orthosilicate formula $R_3''R_2'''(SiO_4)_3$, where

R″=Ca, Fe, Mg, Mn; and R‴=Al, Fe, Cr, or rarely Ti. The following principal types may be distinguished :—

Calcium-iron-garnet	$Ca_3Fe_2Si_3O_{12}$ Andradite
Calcium-chromium-garnet	$Ca_3Cr_2Si_3O_{12}$ Uvarovite
Calcium-aluminium-garnet	$Ca_3Al_2Si_3O_{12}$ Grossularite
Iron-aluminium-garnet	$Fe_3Al_2Si_3O_{12}$ Almandine
Magnesium-aluminium-garnet	$Mg_3Al_2Si_3O_{12}$ Pyrope
Manganese-aluminium-garnet	$Mn_3Al_2Si_3O_{12}$ Spessartite

Only exceptionally is the composition of actual garnet crystals as represented above. As a rule, several, or even all, of these compounds enter into isomorphous mixtures; and whilst there is generally a preponderance of one or other of them, this is not always the case. All the members of the group crystallise in the cubic system, usually with the form of the rhombic-dodecahedron or the icositetrahedron, or a combination of these. The crystals are often rounded or granular in form. There is no cleavage, and the lustre often inclines to resinous in character. Corresponding with the wide range in chemical composition, these minerals exhibit a wide range in colour (yellow, brown, red, green, black, rarely colourless, but not blue), transparency, sp.gr. (3·15 to 4·3), hardness (6½–7½), and mode of occurrence. They occur as primary constituents of igneous rocks; in gneisses, schists, and crystalline limestones; in veins and encrusting the walls of crevices in rocks. Granular rocks composed wholly of garnet are also known.

The chief application of garnet is as a gem-stone, of which there are several beautiful varieties. *Hessonite*, or cinnamon-stone, is a variety of calcium-aluminium-garnet, containing small amounts of ferrous and manganous oxides; its colour is a warm yellowish-red. *Almandine* is deep red, often with a violet tinge. *Pyrope* (Bohemian garnet, 'Cape ruby') is a fiery red. *Rhodolite*, a variety midway between almandine and pyrope in composition, is remarkable for its delicate rhododendron-red colour. *Demantoid* is a calcium-iron-garnet of a rich emerald-green colour and with a brilliant lustre.

Garnet is also used as an abrasive agents mainly in the form of sand, for sawing and grinding stone and for making garnet-paper (often sold as 'emery-paper'). Owing, however, to its lower degree of hardness, it is of less value than corundum and emery. Practically the whole of the massive garnet used for this purpose is mined in the eastern United States, principally New York, but also Connecticut, Pennsylvania, and North Carolina. The output amounts to about 5000 tons per annum, valued at about 6*l*. per ton. In the garnet-mining district of the Mittlegebirge in northern Bohemia, the small material, left after picking out the stones suitable for cutting as gems, is used for gravelling garden walks. L. J. S.

GARNIERITE. A hydrated silicate of magnesium and nickel, of importance as an ore of nickel. It is soft and earthy, greasy to the touch, and usually of a bright apple-green colour; sp.gr. 2·3–2·8. The composition is variable (SiO_2, 35–52; MgO, 2–37; NiO, 2–50; H_2O, 10–20 p.c.), and the material is probably a mixture. It may be regarded as a hydrated magnesium silicate, allied to serpentine, in which variable proportions of magnesium are replaced by nickel. The darker green varieties are sometimes distinguished by the name *noumeite* (from Noumea in New Caledonia), the name garnierite (after Jules Garnier, the discoverer of the New Caledonian nickel ores) being reserved for the lighter-coloured varieties. A chocolate-coloured variety, containing iron, has been called *chocolite* (J. Garland, Nickel Mining in New Caledonia, Trans. Inst. Mining and Metall. 1894, 2, 128, 224). *Nepouite*, from Nepoui, New Caledonia (E. Glasser, Compt. rend. 1906, 143, 1173), is a finely crystalline variety for which the formula is given as $3(Ni,Mg)O·2SiO_2,2H_2O$, the amount of nickel oxide ranging from 18 to 50 p.c.

These minerals occur in veins traversing serpentine rocks in the neighbourhood of Noumea, or Numea, the capital of New Caledonia; and, like the serpentine, they have been produced by the alteration of peridotite rocks, the olivine of which contains traces of nickel. Over 100,000 tons of these nickel ores are exported annually from New Caledonia.

Large deposits, forming beds 10 metres in thickness, of the same type of ores occur, also in connection with serpentines and olivine rocks, at Riddles, in Douglas Co., Oregon. The nickel mineral from this locality is sometimes referred to *genthite*, $2NiO·2MgO·3SiO_2,6H_2O$. Other similar occurrences are met with and to some extent mined at Webster in North Carolina, at Texas and Lancaster Co., Pennsylvania (genthite), at Revda in the Urals (revdanskite), and near Frankenstein in Prussian Silesia (pimelite, alipite, &c.).

On the New Caledonian ores, *see* A. Liversidge, The Minerals of New South Wales, &c., 1888, 275; F. D. Power, Trans. Inst. Mining and Metall. 1900, vol. 8, 426, with bibliography; E. Glasser, Ann. des Mines, Paris, 1903, ser. x. vol. 4, 363. L. J. S.

GAS, AIR. When a current of air is passed over or through a volatile liquid hydrocarbon, such as petrol, gasolene, or benzene, the air becomes charged with a certain amount of the vapour from the hydrocarbon and is rendered inflammable, the mixture being known under the name of 'air gas.' Of the various hydrocarbons that have been tried, petrol has proved to be the most useful, on account of its extreme volatility and freedom from impurities which have a slower rate of evaporation.

Petrol is the first distillate from the crude oil as it comes from the oil well, and consists largely of pentane C_5H_{12}, hexane C_6H_{14}, and heptane, C_7H_{16}, the first liquid members of the great paraffin group of hydrocarbons. It is volatile, and has a flash-point below the freezing point of water: one gallon of petrol, on being vapourised, will give 28·4 cubic feet of vapour, whilst a pint of it poured on a level surface will cover about 80 square feet with an inflammable vapour, through which, on coming in contact with a light, a flame will spread; and 100 cubic feet of air can be made highly explosive by the vapour from a pint of petrol.

Attempts to produce an illuminating gas by carburetting air with the vapour of some volatile hydrocarbon, date back to 1841, and until 1889 the mixture was made rich enough to produce a luminous flame. This meant that a large percentage of vapour was required, but on this

account, and also by reason of the varying quality of the hydrocarbon employed, as well as the inefficiency of the carburettors, it proved very difficult to maintain the production of a gas of uniform composition, with the result that the amount of light obtained at the burners fluctuated. Owing to these drawbacks, the development of lighting by means of carburetted air remained in abeyance until the introduction of petrol of fairly uniform composition for motor-cars and the extended use of the incandescent mantle turned the attention of inventors once more to the possibilities of the process.

Using an incandescent mantle, there is no need for a rich gas, so that the proportion of hydrocarbon vapour can be reduced to a considerable extent, thus doing away with many of the troubles attending the carburation of the air.

If air be passed over or through a vessel containing petrol, the resulting mixture is of very uncertain composition, as at the commencement the more volatile constituents evaporate very quickly, yielding a gas which is far too rich, whilst at the end of the operation, owing to the loss of these lighter portions, the residue does not evaporate at anything like the same rate, so that the air cannot take up the requisite amount of vapour, and the gas is of poor quality. Moreover, when evaporation takes place, a certain amount of heat is absorbed or rendered latent, which reduces the temperature of the petrol in the carburettor, and as the temperature falls, so it evaporates less readily, thus affecting the composition of the mixture. It is essential, for obvious reasons, that a gas supply, whether for heating, lighting, or power purposes, should be as constant in quality as possible, and this has led to the introduction of a host of devices, the aim of which is to secure a gas of definite and uniform composition.

In the majority of air-gas generators in use at the present time, the incandescent mantle is employed to develop light from a mixture of petrol vapour and air so poor in hydrocarbon that it gives a non-luminous but sufficiently hot flame to incandesce the mantle.

When petrol vapour is added little by little to air, it is found that with 1·2 p.c. of vapour, a flame will just travel through the mixture; with 1·5 p.c., the mixture burns under proper conditions; whilst with 2 p.c., the mixture becomes explosive, increases in explosive force up to 2·6 p.c., and gradually diminishes in explosibility until 5 p.c. of the vapour is present, when it becomes non-explosive and burns quietly once more.

It is clear, therefore, that if a mixture of from 1·5 to 1·8 p.c. of petrol vapour with air can be made, such a gas will burn with a non-luminous flame in a properly constructed burner without the addition of more air, and which will be sufficiently heating to incandesce a mantle, whilst it has the enormous advantage that, if through a leak it should escape into the air, the admixture of more air with it renders it non-explosive instead of, as in the case of ordinary coal gas, giving an explosive mixture.

This property was first utilised by Hooker in his safety air gas, and has been the objective of all air-gas apparatus makers since his time, as it enables something like 1400 to 1500 cubic feet of air gas to be made from a gallon of petrol, and yields most economical results, as in properly constructed burners such gas will give about 9 candles per cubic foot consumed with an incandescent mantle.

At the present time, air-gas apparatus may be divided into two classes:

(1) Those which give an air-gas containing over 5 p.c. of the hydrocarbon vapour, and therefore require the addition of air in a Bunsen burner before combustion in the mantle; and

(2) Those in which the percentage of hydrocarbon vapour is under 2 p.c., and the gas is burnt in burners of proper construction without the addition of more air.

To the first class belong such forms of apparatus as the 'Aërogen,' in which the gas is afterwards burnt with a further addition of air. Such forms of apparatus have been in use on the Continent for many years, in some cases being utilised for the lighting of large villages from a central supply station. To the second class belong by far the largest number of generators, such as those made by the 'Non-explosive Gas Co.,' the 'Praed,' the 'Eos,' the 'Safety Light,' the 'National,' the 'Globe,' the 'Loco,' 'Solux,' 'Centenary,' and several others.

In all these forms of machine, the apparatus is designed to automatically mix or evaporate the petrol with air in the right proportion, no matter whether it supplies a large or small number of lights, and in order to do this it is useless to employ carburettors in which a current of air flows over the surface of or through the petrol, and the best results are obtained by introducing small quantities of petrol into a carburettor of suitable form, where it meets with exactly the amount of air necessary to vapourise it entirely, producing the gas of the required composition. This is done in several ways. In one type of apparatus, a current of air is forced by a fan driven from a hot-air engine through the carburettor, where it meets with the supply of petrol, which is pumped up from a storage tank below the apparatus, and entering the carburettor at the top in the right ratio to the air supply is injected into the current of air as a spray, thus ensuring immediate volatilisation.

In another type of machine, the flow of petrol to the carburettor is regulated by a mercury valve contained in a chamber outside the carburettor. As the level of the petrol in the carburettor sinks, so the mercury seal is opened, allowing more petrol to flow into the carburettor in just sufficient quantity to replace the loss. In a third system, the air is forced in through a rotating meter, the revolving spindle of which works the regulator of the petrol tank. In the carburettor, the petrol flows on to the surface of a sphere or ball, round which the air is made to circulate in such a way as to completely evaporate all the petrol, the mixture being, at the same time, well agitated by a fan to ensure thorough mixation and uniformity of composition.

Another form of apparatus consists of a multi-chambered turbine arrangement. The petrol and air in definite quantities are admitted into each chamber in succession, and violently

agitated therein, with the result that the petrol is almost instantly vapourised, the carburetted air being discharged into a central mixing chamber into which the gas from each chamber flows before it passes off to the holder.

The motive power for the production of the necessary pressure of air can be obtained by the slow descent of a weight, by water power, or, most generally, by a hot-air engine actuated by the combustion of a small portion of the air gas itself.

The drawback to the use of a falling weight is that, unless an abnormal length of fall be arranged for, its period of working is comparatively short before it requires winding up again. Water is reliable, and serves well where a supply is available, but the cost is high if it has to be paid for. The hot-air engine as now made consumes but a very small amount of gas, and is of simple yet reliable construction: it runs noiselessly, and can keep at work for indefinite periods with the minimum of attention.

The burners employed for the combustion of the air gas naturally vary with the quality of gas made, as with gas containing below 2 p.c. of vapour no admission of air before combustion is needed, and the burners have to be packed with small tubes or wire gauze, so that if by any chance an explosive mixture is formed in the generator, owing to the amount of petrol vapour having risen to over 2 p.c., flashing back to the regulating apparatus, and so causing an explosion, would be prevented: with those machines which give a mixture richer than 5 p.c. in vapour, a burner of the ordinary Bunsen type, capable of very delicate adjustment, has to be employed, but in no case must an apparatus be installed in which there is no arrangement, such as a safety chamber, between the burners and the regulating drum for the prevention of a flash-back.

With regard to the installation and distribution of the gas, owing to its sensitiveness to atmospheric conditions, great attention should be paid to the arrangement of the falls in the pipes, and siphons should be inserted where there is any chance of a deposit accumulating. It is an advantage to use pipes of rather larger diameter than would be adopted for coal-gas lighting, especially for installations producing a weak gas, as the volume of gas consumed per candle power is more than double that of coal gas, but existing pipes can be utilised in many cases, providing they are not less than $\frac{3}{4}$ inch in bore. As regards the fittings, the ordinary coal-gas fittings can generally be employed, provided the gas way is of sufficient size to be consistent with the extra volume of gas consumed.

The heating power of air gas is of course dependent upon the percentage of petrol vapour which it contains, and as the different commercial makes of petrol, benzene, &c., which could be employed in such plants vary, it is necessary to know not only the percentage of petrol vapour present, but the source of such vapour. The variation in heating power of the carburetting material used in air-gas machines and internal-combustion engines, is shown in the following table:—

CALORIFIC VALUES (NET).

(W. Watson.)

Petrol	Density at 15°	Calorific value (net)			
		Cals. per gram	Cals. per c.c. at 15°	B.Th.U. per lb.	B.Th.U. per gall. at 15°
Bowley's special	0·684	10,660	7290	19,190	131,500
Carless . .	0·704	10,420	7340	18,760	132,300
Express . .	0·707	10,020	7080	18,040	127,600
Ross . .	0·714	10,370	7400	18,670	133,600
Pratt . .	0·719	10,340	7430	18,610	134,100
Carburine .	0·720	10,380	7470	18,680	135,000
Shell (ordinary)	0·721	10,400	7500	18,720	135,300
Dynol . .	0·725	10,290	7460	18,520	134,600
Simcar benzol .	0·762	9,490	7230	17,080	130,400
0·760 shell .	0·767	10,140	7780	18,250	140,300
Coaline . .	0·846	9,270	7840	16,690	141,500
Pentane . .	0·630	10,230	6450	18,410	116,300
Hexane . .	0·680	10,430	7090	18,770	127,900
Heptane . .	0·736	10,400	7650	18,720	138,100

If, therefore, 1500 cubic feet of air gas be made from 1 gallon of Pratt's spirit, it is clear that the calorific value of the gas will be $\frac{134100}{1500}$, or 89 British thermal units per cubic foot.

V. B. L.

GAS CARBON *v.* CARBON; also GAS, COAL.

GAS, COAL. During the 17th and 18th centuries, several observers noticed the evolution of combustible gas in the neighbourhood of coalfields, which burned with a luminous flame, and also that a gas of this nature was produced by the distillation of coal in closed vessels, but the first to carry out the process of the distillation of coal for the special purpose of producing a gas for use as an illuminant was William Murdoch, who, in 1792, lighted his house at Redruth by this means. At that time, Murdoch was in charge of James Watt's condensing steam engines recently erected at Cornish mines by Messrs. Boulton and Watt, of which firm he was the representative, and on returning later to the works of Messrs. Boulton and Watt at Soho, Birmingham, he continued his work on the subject, and, probably in 1798, lighted a part of the works with coal-gas. Independently of Murdoch, but at a rather later date, Philippe Lebon of Paris also employed for lighting purposes the gas evolved by the distillation of wood, the date of his first patent being 1799.

From 1803 onwards, installations of coal-gas plant were introduced for lighting various houses and factories, largely by Murdoch and Boulton and Watt, but they do not appear to have contemplated the erection of works for a public supply of the gas, although this plan had been advocated already by Lebon. F. A. Winsor or Winzer, a native of Moravia, had become acquainted with Lebon's ideas when in Paris, and on settling later in London, he commenced an agitation for the foundation of a company there for the manufacture and supply of coal gas, and marred though his efforts were by gross extravagance of statement and unjustifiable claims, they were nevertheless eventually successful in 1810 in the obtaining of an Act of Parliament for the formation of a Statutory Company in London, which two years later received a charter of incorporation,

and still continues under the name of the Gas Light and Coke Co., London.[1]

From this time forward, the manufacture and public supply of coal gas has steadily increased, but until the last quarter of the 19th century, the coal gas was almost exclusively employed for illuminating purposes, by utilising the luminosity developed by burning it in open flames, and the quality of chief importance was its illuminating power. During the last 30 years, however, the conditions have completely altered, owing to steadily increasing employment of the gas for the purposes of heating and cooking, and for the production of power by its use in gas engines, for which purposes the calorific power of the gas is the chief factor of importance. Moreover, since the introduction of the incandescent burner by Auer von Welsbach in 1887, this method of lighting, in which a mantle composed of thoria and ceria is heated to incandescence by a Bunsen flame, has, to a very great extent, replaced the open flame burners, the number of which is still steadily decreasing, probably less than 10 p.c. of the gas supplied being now thus used. With the incandescent burner, the light evolved is dependent mainly, though not entirely, on the calorific power of the gas, but has no direct connection with its illuminating power when burnt in open flames, so that at the present time, for so far as the great bulk of the gas supplied is concerned, its calorific power is the property of primary importance.

During the last 40 years, great progress has also been made in the manufacture of gas having low illuminating power, and containing a large proportion of inert gases such as nitrogen and carbon dioxide, but which can be produced at a low price and has still sufficient calorific power for employment in gas engines and for furnace heating, and such gas is now also produced in very large quantities, being, in most cases, manufactured at the works where it is required, and not distributed from a central station (*see* FUEL). Here, however, only the production of what is ordinarily known as 'coal gas' will be considered, that is, the gas distributed for public use and capable of being employed at the desire of the consumer for lighting, heating, or power purposes. The magnitude and extent of this industry and the manner in which it has extended during the past 24 years is shown in the following table, giving the summary of the figures in the Board of Trade returns from all authorised gas undertakings belonging to statutory gas companies or local authorities for the years 1885 and 1909.

—	Capital or loan authorised	Paid up and borrowed	Tons of coal carbonised	Number of cubic feet of gas made	Number of cubic feet of gas sold	Length of gas mains in miles	Number of consumers	Number of public lamps lighted
	£	£		thousands	thousands			
1885 .	71,863,267	35,513,570	8,378,904	84,637,727	77,393,670	18,967	2,095,025	402,074
1909 .	154,500,093	132,123,284	15,225,320	193,547,394	177,686,943	35,230	6,164,066	712,903

This table does not include the production of some private companies, but their total output is very small, and would not materially affect the figures.

In addition to the gas output, coke, tar, and ammonia are also produced in large quantities as by-products. The exact figures for coke and tar are not available, but approximately 6 to 7 million tons of coke and 150,000,000 gallons of tar are now sold annually from gasworks alone. The production of ammonia from gasworks in 1909, calculated as sulphate, was 164,276 tons.

Principles of manufacture. Up to within the last few years, the method of manufacture of coal gas has remained in its general principles almost identical with that employed by Murdoch and his immediate successors (prominent among the latter being Samuel Clegg, senr., and his son, Samuel Clegg, junr.), although in detail and in the magnitude of the operations, great change has taken place. So far as the actual carbonisation of the coal is concerned, Murdoch, after experimenting with different types of retort, settled down to the employment of long, narrow retorts set horizontally, into which the coal was charged all at once in such a manner as to leave a free space above the coal throughout the whole length of the retort, the charge being then allowed to remain in the retort until it was completely carbonised, when the residual coke was raked out and the retort recharged with coal; and this plan is still the one employed in the great majority of cases. At first, cast-iron retorts were used, but the rapid wearing out of these, especially when the temperature of carbonisation was increased, soon led to the substitution of fireclay for cast iron, and such fireclay retorts have long been in universal use, except in a few very small works.

The further treatment of the hot volatile products issuing from the retorts to obtain a gas suitable for distribution, still generally follows the lines adopted in the earlier days of the industry. These products are first cooled to approximate atmospheric temperature, when the condensible vapours liquefy, forming tar, and the steam always present in quantity condenses to water, the latter then dissolving part of the ammonia present in the gas as well as other gaseous impurities, especially sulphuretted hydrogen and carbon dioxide. The remainder of the ammonia is removed by washing with water (wet purification). For the further purification of the gas, the latter, after removal of the ammonia, was in the earliest stages of the industry passed through milk of lime, which removes the whole of the sulphuretted hydrogen and carbon dioxide, and some of the carbon disulphide present in small amount, but the use of milk of lime was soon replaced by that of slaked lime in a slightly moist condition (dry purification), placed in

[1] For a full account of the early history, *see* A History of the Introduction of Gas Lighting, by C. Hunt (Walter King).

layers in a closed purifier constructed in such a manner that the gas filtered through successive layers of this material. At a rather later date, hydrated ferric oxide, placed in similar purifiers, was employed for the removing the sulphuretted hydrogen, the carbon dioxide being then either separately removed by lime or allowed to remain in the gas.

After the coal-gas industry became firmly established, there was, as already stated, for a long time no material alteration in principle in the manufacture, but very considerable changes took place in the details of the plant and in the construction of apparatus of large size to deal with the constantly increasing demand. Until about 1880, gas undertakings were subjected to but little effective competition from other means of producing artificial light, especially in towns, but from that time, competition has steadily increased, on the one hand from the electric light, and on the other from the introduction of cheap mineral burning oils, and the stimulus of effective competition has resulted in a much more rapid advance, both in the technical aspects of the manufacture of the gas and in the commercial methods adopted in its sale.

The technical advances have, until recently, involved no great alteration of principle, and have consisted generally in improving the efficiency and economical working of the plant employed, and in the introduction of mechanical transport for the large quantities of material which have to be dealt with, including the adoption of labour-saving machinery. Further, the temperatures at which the coal is carbonised have been increased, resulting in a larger yield of gas per ton of coal, and although such gas is of lower illuminating and calorific power, the falling off is much less than the increase in yield, especially as regards the now more important quality of calorific power. In consequence of these changes and the increased use of gas for other purposes than that of lighting, which has resulted in a more uniform demand for gas over the 24 hours of the day and in the summer and winter months, the price of gas has, on the average, steadily fallen, in spite of the fact that the cost of the raw materials and the rate of labour remuneration have risen considerably.

The actual price varies very much, according to local conditions, such as the magnitude of the works and its distance from suitable coal supplies, and also with the character of the financial and technical administration of the undertaking, both in the present and in the past. At the present time (1912), the lowest price charged is 1*s.* 2*d.* per 1000 cubic feet for general purposes and 1*s.* per 1000 cubic feet for power purposes, and except in the case of small undertakings at a distance from the coal-fields, the price now rarely exceeds 3*s.* 6*d.* per 1000 cubic feet.

In the United States, following on the development of the Pennsylvanian oil-field and resulting cheap oil supply, the manufacture of coal gas was largely superseded by that of carburetted water gas, that is, of a mixture of water gas and oil gas of approximately the same illuminating power as coal gas, and now about 80 p.c. of the gas supplied consists of carburetted water gas; the present tendency there appears, however, to be in the direction of a recovery in the percentage of coal gas produced. In this country also, since 1890, carburetted water gas has been largely manufactured in many undertakings, and mixed with the coal gas to an extent which mostly does not exceed 40 p.c. of the total output of the works making such gas. During the year 1909 the total production of carburetted water gas in the United Kingdom amounted to rather more than 12 p.c. of the total output.

Gas coal. In this country, by far the largest proportion of coal employed for gas-making purposes is of the character known as bituminous caking coal, *i.e.* a coal which, in addition to yielding a large volume of gas, also forms a plastic mass during the early stages of heating, and then subsequently undergoes carbonisation, and results in the production of a coherent coke of good commercial value. The non-caking bituminous coals, even when yielding a large volume of gas, only give a poor coke, having the same shape and size as the pieces of coal carbonised, and having a low selling value. These are therefore only employed in cases where local conditions are such that non-caking coals are obtainable at a cost sufficiently below that of caking coals, to compensate for the lessened value of the coke produced. This is especially the case in Scotland, where the Scotch splint coals are of a non-caking or only feebly caking quality.

A further exception to this rule also occurs in the case of cannel coal, which was formerly used in considerable quantity, as, although the coke obtained was almost useless, it gave a very large yield of gas of high illuminating power, and a certain proportion of cannel was therefore used in many works to enrich the gas given by poorer coals to the statutory quality. At the present time, however, very little cannel is employed: firstly because, the increasing scarcity of good cannel caused a rapid increase in its price some 20 years ago, on which account oil from petroleum was largely used in its stead for enrichment, either by making this into oil gas or carburetted water gas and adding these gases to the coal gas. In place of the use of cannel, the low-quality gas was also frequently enriched by carburetting with volatile hydrocarbon vapours, such as the low-boiling paraffins and benzene. In the second place, owing to the lessened importance of illuminating power, enrichment of the gas has now been largely given up, and, except in many Scottish undertakings, the illuminating power has now mostly been reduced to such a figure as can be obtained direct from the caking coals most readily procurable in the locality of the particular gas undertaking.

The rich cannel coals were chiefly obtained from the Wigan coal-field in Lancashire and the Lanark coal-field in Scotland, but the supplies are now largely exhausted. Poorer cannels are found to some extent in most of the other coal districts, but these often give little or no better yield and quality of gas than the bituminous coals, and also give rise to a very low quality of coke, and are therefore only used when the price at which they can be purchased is very low.

Structure of coals. The different varieties of bituminous coal are, for the most part, built up of parallel laminations of coal substance, and the appearance and structure of the different

layers in a lump of any such coal differ very considerably; and the following three types of coal substance may generally be recognised. (1) *Charcoal, or 'mother-of-coal,' or 'smut.'* This appears to consist of vegetable matter which has undergone considerable decomposition before deposition, and is soft and presents the fibrous structure of woody matter in a marked manner. (2) *Pitch coal.* This is bright and lustrous, and breaks with a conchoidal fracture and, as its name indicates, closely resembles pitch. Such layers are generally hard and brittle, and, though rich and bituminous in appearance, usually yield poor coke, and contain a good deal of moisture. (3) *Bright bituminous coal.* These layers are very bright and brittle, and have a cubic fracture: the actual thickness of a layer rarely exceeds an eighth of an inch, but they frequently occur together without appreciable parting by other kinds of coal substance, and the coal is then usually of high quality, giving a good yield of gas of high illuminating and calorific power as well as good coke. In addition to the different layers of coal substance, thin layers of mineral matter are of frequent occurrence, these frequently consisting of calcium carbonate or sulphate, or of iron pyrites. All such mineral constituents are disadvantageous, as they increase the percentage of ash in the resulting coke, but the last is especially objectionable, as it also increases the amount of sulphur impurity to be removed from the gas.

Cannel coal is hard and tough and, when broken, shows a smooth or conchoidal fracture, quite different from that of common coal. It has a dull greyish-black colour, and externally appears homogeneous, apart from thin vertical cracks filled with calcareous material or pyrites, but the coke and ash obtained from it show distinct evidence of the existence of horizontal layers. The percentage of ash in cannel coal is on the average much higher than that in common coal, and the coke obtained from it is usually almost valueless in consequence.

Chief sources of gas coals. Gas coal occurs in all the coal-yielding areas, but the chief supplies occur in the Newcastle or Durham district, South Yorkshire, Lancashire, Derbyshire, and North Staffordshire. Smaller amounts are obtained from North Wales, South Wales, and Somerset. Generally speaking, in order to reduce the cost of carriage, a gas undertaking obtains its coal from the nearest field producing a suitable quality. In the London district, however, and also for the most part in the south and south-west of England, the main supply is drawn from the Durham field, the greater distance away of these collieries being more than counterbalanced by the fact that the coal is brought for the greater part of the way by coasting steamers instead of by rail, which reduces the rate of carriage.

The coals obtained from the different seams in the same district, and often even from the same seam, vary considerably in their properties from a gas maker's point of view, and with one and the same sample of coal, the gas results also depend greatly upon the conditions under which it is carbonised. Nevertheless, the coals from each district have, as a rule, certain characteristics which distinguish them from those of other localities. This is especially the case with the coals from the Durham field, these, for the most part, undergoing carbonisation more slowly than the others under similar conditions, and yielding a harder and denser coke. They also yield a thicker tar of higher sp.gr., and in general give a somewhat lower yield of ammonia. The North Staffordshire coals also yield coke of good quality, the gas coke from both these districts being, on the average, superior to that from Yorkshire, Derbyshire, and Lancashire coal.

Valuation of gas coal. The simple elementary analysis of coal, giving the percentages of moisture, carbon, hydrogen, oxygen, nitrogen, sulphur, and ash, affords but very little information as to its value for gas-making purposes. If, however, as first pointed out by Bunte (J. Gasbel. 1888, 31, 895), the figures for moisture and ash be eliminated, and the percentage composition of the actual coal substance calculated, it is possible to judge the general properties of the coal from the figures obtained.

St. Claire Deville published a table (p. 657), giving the results obtained from five typical samples of coal, which were subjected to analysis and gas-making tests in the coal-testing plant of the Paris Gas Works. Coals of Type III. (7·5–9·0 p.c. of O in the coal substance) represent the best type of gas-making coals, giving a good yield and quality of gas and also good coke. Coals of Types I. and II. produce much coke and a poor yield of gas, whilst with Types IV. and V. the gas results are good, but the coke is poor in quality and quantity. The conclusions to be drawn even from such analyses are, however, at most only of a very general nature.

Of greater value and more rapidly carried out is the *proximate analysis* of coal, *i.e.* the determination of moisture, volatile matter, coke, and ash, and, if required, of sulphur, which is objectionable as an impurity. The quantity of volatile matter, *i.e.* loss of weight, exclusive of moisture, when the coal is ignited in absence of air (which gives conversely the percentage of coke), varies according to the manner in which the heating is carried out, and to obtain comparable results a standard method of heating must be adhered to, the one usually adopted now in Great Britain and America being that known as the American method (J. Amer. Chem. Soc. 1899, 21, 1122), which is as follows: 1 gram of undried powdered coal is placed in a bright platinum crucible of 20 to 30 grams weight, closed with a well-fitting lid and supported in such a manner that the crucible bottom is 6–8 cm. above the burner top. An ordinary Bunsen burner, having a flame at least 20 cm. long when burning free, is employed for heating, which is continued for 7 minutes. The upper surface of the lid should be free from carbon at the end of the test, but the under surface should remain covered with a black film. The tests carried out in this manner give yields of coke which approximate very fairly to those found in actual practice in gasworks and coke-oven works.

The quantity of volatile matter, excluding moisture, in gas coals usually varies from about 27 to 35 p.c. of the undried coal, or from 29 to 38 p.c. of the actual coal substance, *i.e.* coal, exclusive of moisture and ash.

	Type I.	Type II.	Type III.	Type IV.	Type V.
100 parts of coal substance contain: Oxygen	5·56	6·66	7·71	10·10	11·70
Hydrogen	5·06	5·37	5·40	5·53	5·64
Carbon	88·38	86·97	85·89	83·37	81·66
Nitrogen (approx.)	1·00	1·00	1·00	1·00	1·00
Moisture content of air-dried raw coal	2·17	2·70	3·31	4·35	6·17
Total weight of distillation products	26·82	31·59	33·80	37·34	39·27
„ „ coke	73·18	68·41	66·20	62·66	60·73
Gas, per cent. coal substance	13·70	15·08	15·81	16·95	17·00
Tar	3·40	4·65	5·08	5·48	5·59
Gas liquor	4·58	5·22	6·80	8·62	9·86
COMPOSITION OF THE GAS IN PER CENT. BY VOLUME.					
Carbon dioxide	1·47	1·58	1·72	2·70	3·13
Carbon monoxide	6·68	7·19	8·21	9·85	11·93
Hydrogen	54·21	52·79	50·10	45·45	45·26
Methane and nitrogen	34·37	34·43	35·03	36·42	37·14
Heavy hydrocarbons	3·27	4·01	4·94	5·58	5·54
Specific gravity of the gas	0·352	0·376	0·399	0·441	0·482
Gas consumption for equal candle power	132·1	111·7	103·8	102·1	101·8

The actual results obtainable from a coal sample can only be determined by tests on the manufacturing scale, and for this purpose arrangements are made in many works by which one or more beds of retorts can be isolated, and the gas passed through special condensing, purifying, and measuring plant, and either the whole or an average sample of the gas collected for testing: the coke, tar and ammoniacal liquor also produced are measured in a suitable manner. In large undertakings, a special testing works is sometimes erected, capable of dealing with quantities of coal up to 20 tons a day. Small-scale plants, modelled to represent large-scale practice as nearly as possible, cannot be relied on to give results obtainable in actual practice, as it is impossible to reproduce the conditions sufficiently exactly; but such plants are of use in giving the *comparative* values of different coal for gas-making purposes, and from tests made with different samples in one and the same plant, a fair idea may be obtained of the *relative* values of different samples. Such apparatus also permits of the checking off of deliveries of coal made under contract to see that they agree with the value obtained from the original sample tested in the same plant.

In order to get a comparative figure of the value of a gas coal, where illuminating power is the chief consideration, the number of cubic feet obtained per ton is multiplied by the illuminating power, this figure being known as the 'multiple.' In some cases, however, this is expressed in 'sperm value,' i.e. the number of lbs. of sperm (as used in the manufacture of the statutory sperm candle), equivalent in light-giving power to 1 ton of coal. This figure is obtained by multiplying the product of yield and illuminating power by 0·00343. For gas-works purposes, the volume of gas is corrected to that of the gas at 60°F. and 30 in. barometer, saturated with moisture.

For calorific power, the product of the yield per ton by the calorific power expressed in British thermal units per cubic foot, is employed, this 'calorific multiple' therefore representing the total yield of British thermal units per ton of coal.

THE MANUFACTURE OF COAL GAS.

The chief manufacturing processes necessarily involved consist briefly in (1) the distillation of the coal; (2) the cooling and condensation of the volatile products; (3) washing the gas for removal of ammonia; (4) purification of the gas from sulphuretted hydrogen; (5) measurement of the gas produced; and (6) its storage in gas holders. The plant required consists of retorts set in suitable furnaces, cooling apparatus for the hot gas, washers, and scrubbers, purifiers, meters, and gas holders, with suitable buildings and accessories.

In order to carry out the manufacture under economic conditions, much depends upon the nature and position of the site. It is not possible to lay down fixed rules with regard to the site to be selected, as generally only a few possible sites are available in suitable positions relative to the district to be supplied, and that which has the least objections to it has to be taken, even if it is by no means ideal. For

works of any magnitude, it is, however, essential that the site shall have a good connection with the means of transport, especially with the railway, and, where possible, also with water, as otherwise the costs for bringing in the large quantities of coal required and sending out the coke produced are largely increased: it is also now the practice, wherever possible, to avoid erecting new works in densely populated districts.

In the laying out of the site it is equally impossible to lay down any but the most general rules, as the conditions vary so greatly in almost every case. The object aimed at is to lay out the works in such a manner that advantage is taken where practicable of the existing natural conditions of level or of the relative position of the railway, canal, or wharf, as the case may be, to facilitate the cheap handling of the raw material and finished products, especially of the coal and coke which form much the largest proportion of these. In spacing out the various

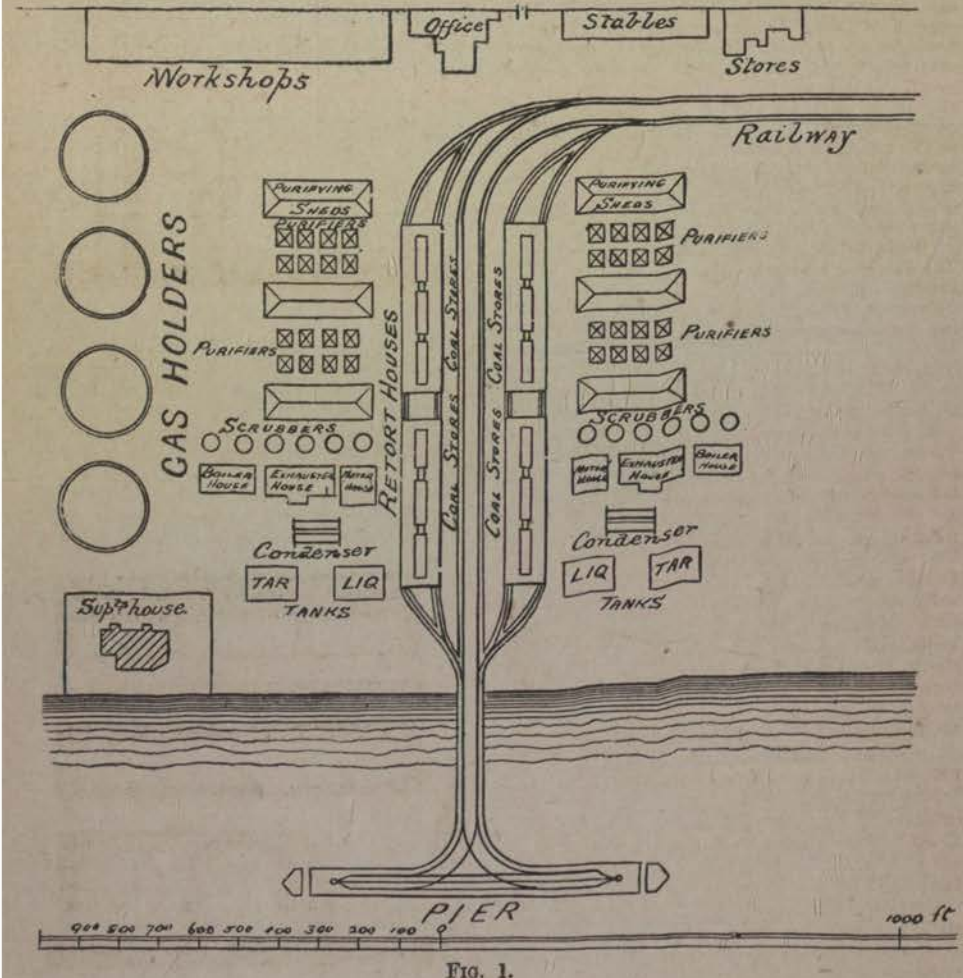


FIG. 1.

portions of the plant for carrying out the different processes, sufficient room should be allowed for each, as undue crowding always tends to increase manufacturing costs. Care must also be taken that the plan is such as to allow of the extension of the various portions of the plant, without necessitating the pulling down and re-erecting of the original plant in a different position or undue cramping of the latter.

Fig. 1 gives a diagrammatic representation of the plan of a gas works capable of making from 10 to 15 million cubic feet of gas per day, and having connection both with rail and water, the works being divided into two completely separate sections, so far as manufacturing plant is concerned; the gas from each section, however, joins together at the inlet to the gas holders, which can be filled from either section. It very rarely happens, however, that the disposition of the site renders so symmetrical an arrangement possible.

CARBONISATION OF THE COAL.

Broadly speaking, the process of carbonisation, which is by far the most important part of

the manufacture, consists in subjecting the coal to distillation in closed vessels from which air is excluded, whereby it is split up into two portions, namely, a volatile portion which escapes from the retort, by subsequent treatment yields tar, ammoniacal liquor, and permanent gas, and a non-volatile portion consisting mainly of carbon and the ash of the original coal, which remains behind in the retort as a porous mass of coke. The nature and amount of the constituents of the volatile products, as well as the composition and physical properties of the residual coke, depend not only on the nature of the original coal, but also to a large extent on the temperature employed for its carbonisation and on the manner in which the heating is carried out. The nature of the physical and chemical changes which occur is exceedingly complex, and these, so far as they have at present been elucidated, will be more conveniently considered after a description of the actual process of carbonisation as it is at present carried out in the great majority of gas works.

Manufacture of gas in horizontal retorts. The material employed for the manufacture of retorts consists at the present time almost universally of fireclay, and for modern carbonising conditions, the quality of the latter should be such that it will withstand temperatures up to 1300°–1400°, and should not develop serious cracks when subjected to such rapid alternations of temperature as inevitably occur when the hot retort is recharged with a cold mass of coal. The shape of the retorts is long and narrow, the length being from 9 to 10 feet when the retort is closed at one end, or from 18 to 20 feet when a 'through' retort is employed, closed by a mouthpiece and lid at each end, this being now the plan mostly adopted in works of medium and large size. The width of the retort varies usually from 18 to 25 inches and the depth from 13 to 16 inches, the size 16-inch by 22-inch being probably used more than any other. The shape of cross section employed varies very considerably; in a few instances, circular retorts are employed (to which, of course, the above-mentioned dimensions of width and depth do not apply), in others oval retorts, but the majority have now a flat bottom and circular top and have approximately the shape of a half-inverted D, ⊓, and are commonly known as D-retorts, the corners between the bottom and sides being, however, always rounded, to facilitate the removal of the coke, and to render the retort less liable to crack. The thickness of the retort wall is 3 inches, increased to 4 inches at the end to facilitate the fixing of the iron mouthpiece and lid.

A number of these retorts are fixed horizontally in a single brickwork arch, the number in such a setting varying generally from 6 to 12. The retorts are supported by transverse brick walls, placed at intervals throughout the length of the retort, and extending to the top of the arch enclosing the setting, the method of construction being clearly shown in Figs. 2, 3, 4, and 5, which give diagrams showing the cross section and three longitudinal sections of a bed of eight through retorts. The gases by which the retorts are heated circulate around the retorts in each of the vertical chambers formed by the cross walls, travelling first upwards along the inner sides of the retorts, and thence over the top of the highest retorts and down along the outer sides of the retorts and away to the chimney.

The method formerly adopted for heating was that of direct firing, a shallow coke fire being maintained on a hearth placed in the centre of the setting below the middle retorts. With such firing the heating of the retorts is

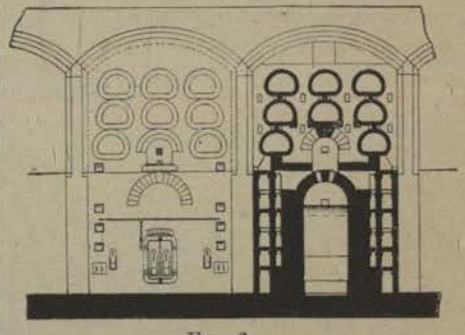


FIG. 2.

effected solely by the sensible heat of the products formed by the combustion of the carbon of the coke by the oxygen of the air, *i.e.* carbon dioxide, nitrogen, excess of oxygen, and in order to get the retorts properly heated in the part with which the gas last comes in contact, it is necessary that the temperature of the latter must not be below about 1000° when they pass away from the setting. As in addition, a considerable excess of air must be used

FIG. 3.

to get complete combustion of the coke, this excess of air likewise passes away to the chimney at a high temperature, resulting in great waste of fuel, and the actual consumption of coke for heating such direct-fired settings amount to 25–30 p.c. weight of coal carbonised.

At the present time, in installations of any size, this method of direct firing has been abandoned in favour of gaseous heating. For this purpose, a deep producer is provided for each bed of retorts, as shown in Figs. 2 to 5, which is charged with hot coke, when required, by allowing the incandescent coke from the

retorts to fall directly into it. A limited supply of air (primary air) is admitted below the furnace bars, and passing through the deep layer of coke, the oxygen is converted chiefly into carbonic oxide and to a smaller extent into the dioxide. Steam is introduced along with the primary air, as water is allowed to drip on to the furnace bars to prevent their burning through, and water also evaporates from that kept in the

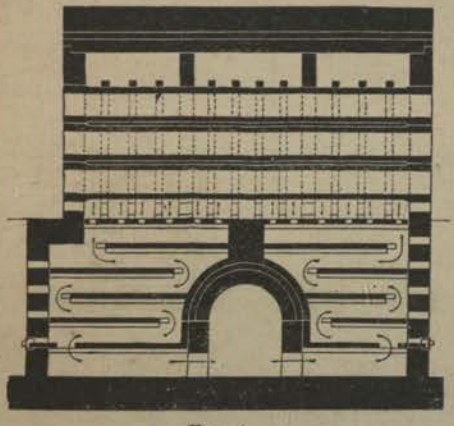


FIG. 4.

ashpan below the surface, and this steam is largely converted into hydrogen and carbon monoxide in passing through the incandescent fuel. The presence of steam lowers the temperature of the fuel in the generator, thus reducing wear and tear of the lining, and also prevents the fusion of the clinker formed from the ash, and renders it more readily removable. The composition of the gas varies according to the

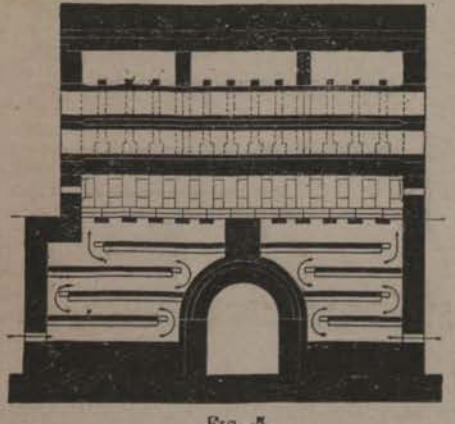


FIG. 5.

proportion of air and steam used, but generally approximates to the following example :—

Carbon dioxide . . .	5·2 p.c.
Carbon monoxide . .	24·4 „
Hydrogen	8·6 „
Methane	0·8 „
Nitrogen	61·0 „

The producer gas thus obtained consists to the extent of about two-thirds of incombustible gases, and is not an ideal one for obtaining very high temperatures; but it is, nevertheless, fully capable of developing the highest temperature required for carbonisation—this being made more easy by reason of the fact that it enters the setting already heated to a very high temperature. Further, as will be seen directly, the air required for its combustion also enters the setting at a moderately high temperature.

In very brief outline, the method of working the setting is as follows: The hot furnace gas collects above the coke, and then passes through nostril holes cut in the furnace arch; one or more nostril holes being placed at the bottom of each of the vertical spaces formed by the cross walls supporting the retorts (*see* Figs. 2 to 5). As it enters the setting, the furnace gas is met by the stream of secondary air necessary for its complete combustion; this being introduced by suitable flues so arranged that a supply of air meets each stream of furnace gas issuing from the nostrils in the furnace arch. Complete combustion of the gas takes place as the streams of furnace gas and air intermix in their circulation around the retorts; the heat thus evolved causing the temperature of the latter to be raised to the required point.

The waste gases leaving the setting have inevitably a high temperature, as they must be sufficiently hot to raise the temperature of the last portions of the retort with which they come in contact to the carbonising temperature required, and if allowed to pass direct to the chimney much loss of heat would ensue. To effect a partial recovery of this heat, the waste gases, on their way to the chimney, pass through the regenerator, which consists essentially of a series of flues adjacent to and separated by a thin fire-brick partition from a parallel set of flues through which the secondary air is allowed to flow on its way to the setting, travelling in the reverse direction to the waste-gas stream. Much of the heat of the latter is thereby transferred to the secondary air, and thus carried back into the setting, resulting both in economy of fuel and enabling a higher temperature to be obtained with a low fuel consumption than would otherwise be the case.

The amount of primary air admitted to the furnace and of secondary air to the setting is controlled by suitable slides on the ports of admission and by dampers placed at the outlet of the regenerators. In a setting of through retorts, these last are usually four in number, each taking the waste gas from one quarter of the setting, so that by their adjustment, not only is the total amount of gases drawn through the setting controlled, but also the proportionate amounts drawn into the different parts. By suitable regulation of the primary air slides and dampers, the furnace is made to produce the requisite quantity of gas for the proper heating of the setting, and the secondary air slides are adjusted to supply as nearly as practicable the exact quantity of air required for the complete combustion of the furnace gas. With this method of heating the fuel, consumption is reduced to about one-half that required with direct firing, viz. from 12 to 15 p.c. of the weight of the coal carbonised, whilst simultaneously much higher retort temperatures are attainable.

The charging of the coal into the retort and

the withdrawal of the coke produced were formerly always effected by manual labour, the coal being charged with the shovel, or by a scoop run into the retort by hand, and then inverted and withdrawn, the coke being drawn by a rake. This plan is still adopted in small works, where the magnitude of the operations is not sufficient to make the installation of machinery remunerative. In larger works, however, the operations are now usually effected mechanically, a considerable number of machines of different type being at present in use. Limitations of space, however, prevent anything more than a very general description of these machines. In the earlier machines, which were widely adopted, namely, the West and the Arrol-Foulis machines, the existing manual method was closely imitated by mechanical means, the charging machine for the coal inserting the latter by means of a scoop or similar contrivance, and the discharger removing the coke by a mechanically actuated rake; in the West apparatus, compressed air is used as the motive power; and in the Arrol-Foulis, hydraulic pressure. In more recent types of machine different methods are employed. Thus in the De Brouwer apparatus, a stream of coal is projected into the retort at such a high velocity that it is carried to a stop placed at the far end, and then built up in an even layer to the front of the retort; in place of raking out the coke, the plan now being adopted is that of mechanically pushing out the coke from one end, this method being, of course, only applicable to through retorts, which can be opened at each end. Other machines, such as the Fiddes-Aldridge, are also in use, which effect in one movement the discharge of the coke and the introduction of a fresh charge of coal, and at the present time electrical power is largely employed for actuating retort-house machinery.

In addition to the actual machinery employed for charging the coal and drawing the coke, additional mechanical equipment is also required in the retort house. The coal to be carbonised must not contain lumps of too large a size where machine charging is used, and is therefore dropped into a coal breaker, from which it falls into an elevator, and is raised to a height well above the retort benches, falling from the latter either direct or by means of a conveyor into storage bunkers, from which it is drawn by the charging machines as required. Mechanical conveyors of various types are also frequently employed for removing the coke from the retort house as it is discharged from the retorts, and to carry it to suitable screening machinery for sorting into different grades.

Inclined retorts. In order to utilise the action of gravity in charging and discharging retorts, the horizontal position of the retorts has been abandoned in many installations during the past 25 years, the retorts being set instead at an angle of about 32° to the horizontal, this being approximately the angle of rest of broken coal. Fig. 6 shows a longitudinal section of such a setting of inclined retorts. To charge them, a stop is placed at the lower end of the retort, and a stream of coal admitted at the top, which falls down the retort until it reaches the stop at the bottom, after which, with a properly regulated supply of coal, it builds up in an even layer to the top of the retort. To discharge the retort after carbonisation is complete, the stop is withdrawn from the bottom, when the coke should fall out by the action of gravity. Usually, however, a certain amount of assistance is required to start the movement, such as pricking with a bar, this being especially the case with retorts which have been at work for some time and have altered in shape.

Inclined retorts were first adopted with practical success by Coze at the Rheims Gas Works in 1885, and have since been installed to

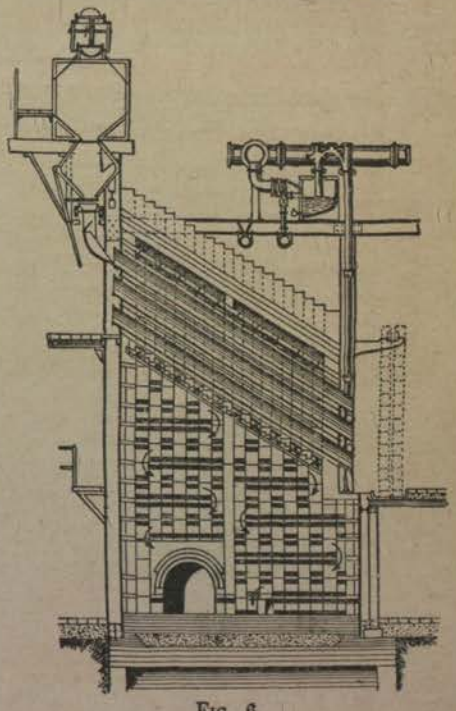


FIG. 6.

a very considerable extent in most countries where the gas industry is established, including Great Britain. Here, however, it has never appeared probable at any time that the inclined retorts would altogether supplant the horizontal retorts, and during recent years but few new installations have been built, the improved machinery for charging and discharging the horizontal retorts having increased the favour with which these are regarded.

The relative advantages of the two systems refer almost exclusively to questions of capital cost, upkeep, and labour charges, and do not materially affect the matter of the yield and quality of gas, as the actual carbonisation of the coal, with proper working, takes place in the same manner in each case, the coal in both being heated in an even layer in the retort, with a considerable amount of free space above the coal, and the sequence of changes which take place from the action of heat are substantially the same in both cases.

Retort-house working. The weight of coal introduced into the retort varies naturally according to the size of the latter, but up to

within the last few years the weight of charge placed into the retort of the most common size, namely, 20 feet long, 16 inches deep, and 22 inches wide, was between 6 and 7 cwts. (and a proportionate charge in retorts of other sizes); and with such a charge, even with coals which swell considerably during carbonisation, a sufficient amount of free space remained above the mass at the end to permit of the introduction of the rake-head to discharge the coke. The temperature within the retort varies in different works from about 900° to 1250°, the tendency being constantly in the direction of the higher figure, and the time required for the carbonisation of such a charge averages about 6 hours in the case of most caking bituminous coals, but is only about 4 hours with Scotch splint coals. The gas evolved during the first half-hour is somewhat low in quality, but in the succeeding 1½–2 hours the yield of gas is highest both in quality and quantity. For the remainder of the time, the volume and quality steadily diminish, and when carbonisation is nearly complete, the small volume of gas evolved consists largely of hydrogen, with from 10 to 20 p.c. of methane and some carbonic oxide. In order, therefore, to obtain a stream of gas which is approximately uniform both in quantity and quality, and also to facilitate retort-house working, the retorts are not all charged together, but a certain proportion only are charged at regular intervals of an hour or two hours, according to circumstances, so that the carbonisation in the different retorts is at different stages at any particular time, and the mixture of gas formed by the combined streams from the retorts keeps more nearly uniform.

Treatment of the hot gases issuing from the retorts. In order to collect the evolved gases, a cast-iron mouthpiece is bolted to the mouth of

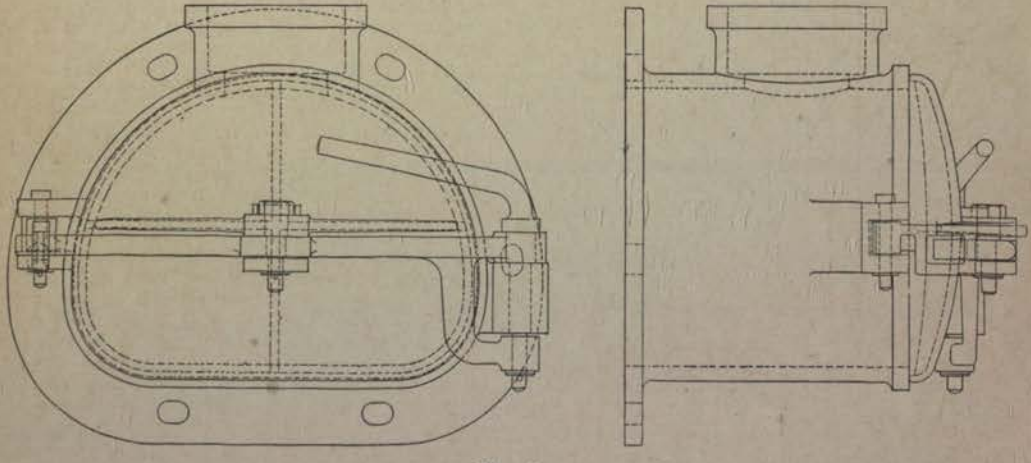


Fig. 7.

the retort (or to both mouths of a through retort) having a hinged lid in front, which can be opened for the purpose of discharging the coke and putting in a fresh charge of coal, and then closed so as to form a gas-tight joint. An illustration of a 'self-sealing' mouthpiece in common use is shown in Fig. 7. On the top of the mouthpiece is cast a socket, into which is fixed a vertical pipe of from 4 to 8 inches diameter, termed the *ascension pipe*, extending upwards above the brickwork of the setting (Fig. 8). By means of the *bridge pipe*, this is connected with the *dip pipe*, which conveys the gas into the collecting main. A separate collecting main is usually now provided for each bed of retorts, the combined gas from each of these passing away by a pipe at the top or side into the *foul main*, by which the gas is conveyed from the retort house to the condensing and purifying plant. Two types of collecting main are in use, namely, the *hydraulic main* and the *dry main*.

In the hydraulic main, which is most commonly employed, the tar and liquor condensed from the gas at this point are allowed to accumulate to such an extent that the dip pipes are sealed in the liquid, this seal then forming an automatic valve, which allows the gas made in the retort to bubble through it into the collecting main, but prevents any gas getting back from that main along the bridge pipe and ascension pipe, when the retort lid is open for purposes of charging. With the dry main the dip pipes are not sealed in the liquid, and in order to prevent gas passing back when the lids are open or air being drawn into the main through the open lid, some method of closing the pipe must be provided which can be operated when the lid is open. Several forms of valve are in use, but are apt to give trouble from the separation of thick tar and carbon on them, and, therefore, in other cases, arrangements are made whereby the dip pipe can be sealed in the liquid whilst the lid is open, and unsealed as soon as this is closed.

Where the hydraulic main is employed, matters are now so arranged in most works that the tar and ammoniacal liquor which separate in that main, are drawn off separately, the tar being taken away from the bottom as it separates, whilst the liquor flows away from an overflow, the height of which can be regulated as desired, the object especially aimed at being to ensure that the dip pipes are sealed in liquor, and not

in tar or varying mixtures of tar and liquor. This separate removal of the tar and liquor may be effected in many different ways, a type of apparatus in common use being the Dillamore tar tower, shown in Fig. 9. This is placed at the end of a bench of retorts as shown, and serves a number of beds. The tar pipe runs from the bottom of each hydraulic main to about the

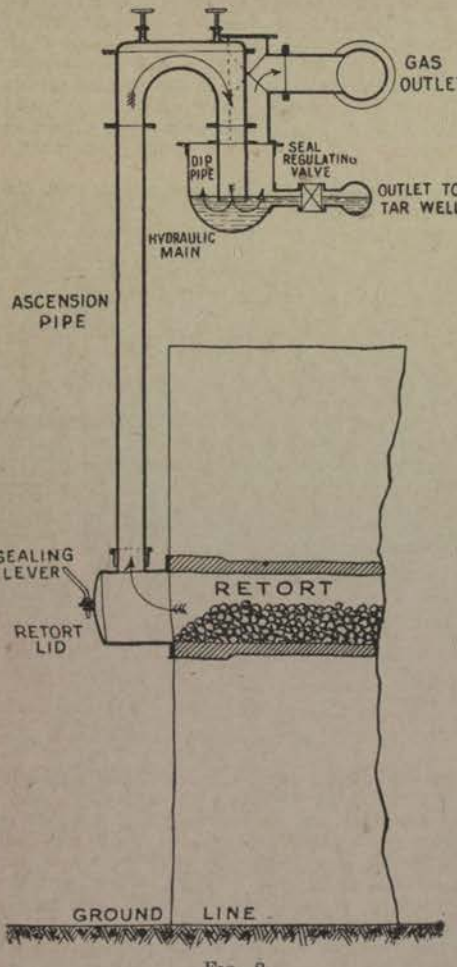


FIG. 8.

middle of the tower, whilst the lighter ammoniacal liquor flows from a side opening near the upper level of the liquid in the hydraulic main to the top of the tower. The latter is also connected by an equilibrium pipe to the top of the hydraulic main, or foul main, the gas pressure in each being thus maintained the same, under which circumstances the upper level of the liquid is the same in both. The condensed liquor flows from the top of the tower over a weir valve, the height of which can be regulated to give any required depth of seal in the hydraulic main. The tar accumulates in the bottom of the tower, displacing an equal volume of liquor, which flows away over the weir valve, and is run off periodically, care being taken that its upper level never rises above the level at which the tar enters the tower. Whilst running the tar off, liquor must be run in from a tank to the top of the tower at a greater rate than that at which the tar is run off, as otherwise the level of the liquid in the hydraulic main would fall, unsealing the dip pipes.

In order to obtain good results in carbonisation, so far as yield and quality of gas are concerned, it is most essential that the gas pressure in the retort should be maintained as uniform as possible, and only slightly above that of the atmosphere, attention to this point being second only in importance to that of keeping good and even temperatures of the retorts. The necessity for this arises from the fact that the fire-clay retorts are themselves porous, and also develop cracks through the alternate heating and cooling, and hence, if the pressure within the retort exceeds that of the gases circulating round it to heat it, gas tends to escape through the pores and cracks, and is burnt around the setting and thus lost; and if, on the other hand, the pressure within the retort is materially lower than that within the setting, waste gases, consisting chiefly of nitrogen and carbon dioxide, are drawn into the retort and pass away with the gas made, and lower its quality. In passing over the hot retort walls, the gas, however, always undergoes a certain amount of decomposition, resulting in the deposition of carbon on the walls, which tends to block the pores and small cracks, and thereby to render the retort more gas-tight, the leakage being much higher with a new retort, or immediately after the removal of the crust of 'gas carbon' or 'scurf.' The latter process must be carried out periodically, as it otherwise becomes so thick as to interfere with the proper heating, as well as with the charging and discharging of the retort, the gas carbon obtained finding a ready sale for the manufacture of electrodes.

A very considerable pressure is required to pass the gas through the condensers, scrubbers, and purifiers, and into the holders, and if the whole of the necessary pressure were thrown on the retort, most of the gas would, in large works, be lost into the setting, and, therefore, in all but very small works a pump or exhauster is employed to draw the gas from the retorts as it is made, and to force it on through the subsequent apparatus and into the holders. The exhauster is run in such a manner as to maintain the gas pressure constant in the hydraulic main above the liquor level, and in addition an automatic retort-house governor is also frequently employed to ensure that this pressure is maintained as uniform as possible. Even then, in order to ensure that the pressure in the retort itself is maintained constant, great care must be exercised in maintaining the hydraulic main exactly level, and the dip pipes of equal length, as otherwise the depth to which these are sealed in liquor will vary, and, consequently, the pressure in the retorts, which is equal to that in the hydraulic main less the depth of the seal, will also vary, so that some may be losing gas to the setting and others drawing furnace gas into the coal gas. Where the latter is the case, the pressure in the retorts and ascension pipe is below that of the atmosphere, and,

consequently, when the retort lid is opened, air is sucked into the gas through the ascension and dip pipe, thus further reducing its quality.

Even when the hydraulic mains are level and the dip pipes sealed to an equal extent throughout, and the pressure in the hydraulic main is maintained constant, the bubbling of the gas through the liquid causes a rapid oscillation of the pressure within the retort, which may be considerable. By careful attention and

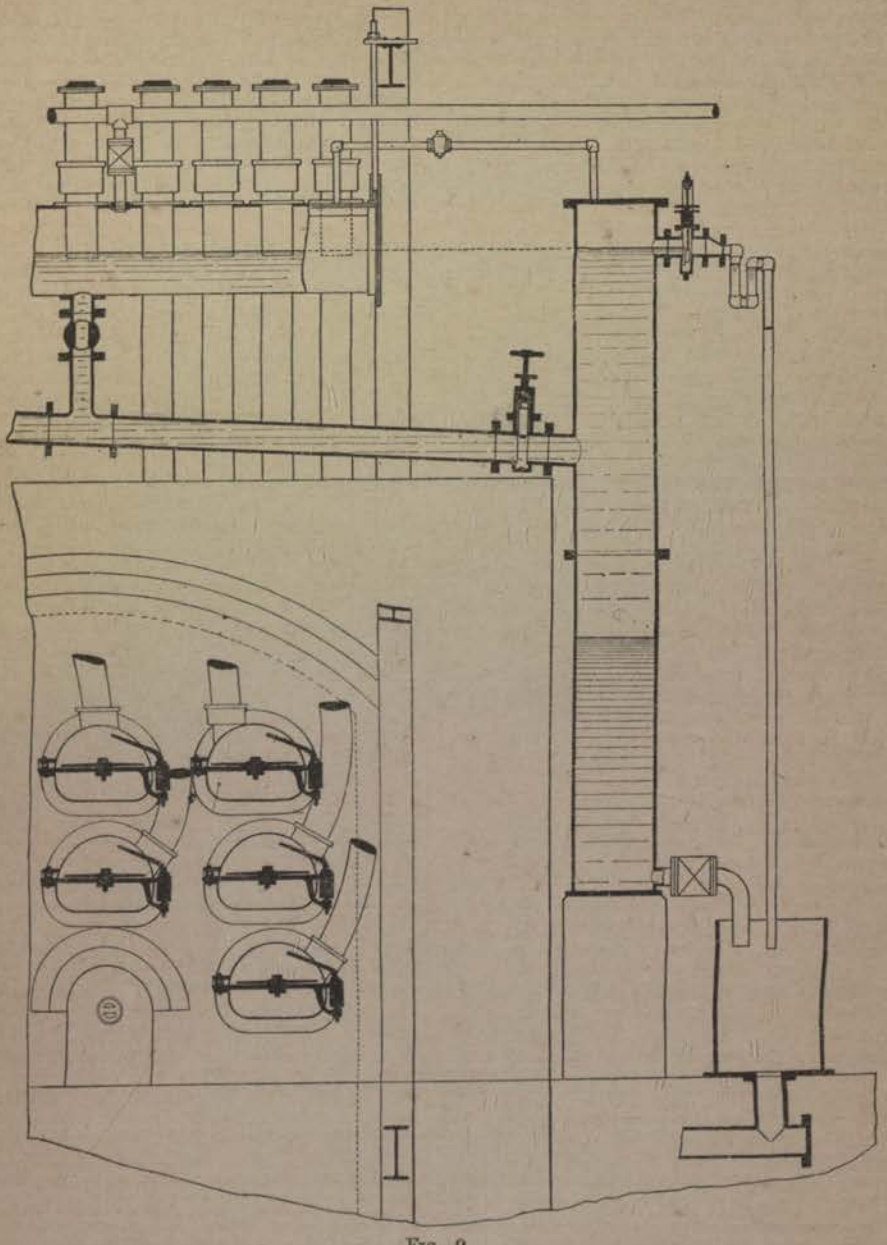


FIG. 9.

regulation of the depth of seal, this oscillation can be very greatly reduced, but never altogether eliminated, and in this respect the dry main, in which there is no seal for the gas to bubble through, has the advantage. On the other hand, the fact that the seal forms an *automatic* valve, which does not require to be operated by the workman when opening and closing the lids, and also that where a dry main is used, more trouble is often experienced in getting the thick tar to flow properly from the mains, especially with some types of coal, has led to the

hydraulic main being most frequently adopted in spite of the above objection.

Chemical Changes occurring during Carbonisation.

The essential elementary constituents of coal are carbon, hydrogen, and oxygen, and, in addition, smaller amounts of nitrogen and sulphur are always present, as well as varying amounts of mineral matter, which remains behind as ash when the coal is completely burnt. With regard to the chemical constitution of the numerous compounds undoubtedly present, very little is known. Various organic solvents extract small amounts of soluble matter, but pyridine extracts very considerable amounts, varying up to about 35 p.c. in the case of coals employed for gas-making (Bedson, J. Soc. Chem. Ind. 1908, 27, 147). Coals which give poor yields of gas also give a low amount of pyridine extract. Burgess and Wheeler (Chem. Soc. Trans. 1911, 99, 649), from their experiments on the gaseous products of decomposition of coal at different temperatures, conclude that coal contains two distinct types of compound, the one, possibly derived from the resins, &c., present in the original vegetable matter from which coal is formed, commencing to decompose at temperatures above 300°, and yielding primarily hydrocarbons, and the other type probably consisting of altered cellulose, only decomposing at temperatures of about 700°–800°, then yielding hydrogen as the chief gaseous product. Good gas-making coals contain a higher proportion of the first class of compounds, and it appears likely that these form the coal constituents soluble in pyridine.

The changes which take place when coal is heated in absence of air are exceedingly complicated in character, and result in the production of an immense number of different substances some gaseous, some liquid, and some solid at the ordinary temperature. The liquid constituents, which condense together in the form of coal tar, are by far the most numerous, the different compounds isolated from it already being numbered by hundreds, and doubtless large numbers of unknown compounds are also present (*v.* Tar). Moreover, both the nature of these substances and their relative amounts in the products vary greatly according to the temperature to which the coal is heated, and the manner in which the heat is applied, and our knowledge of the nature of the reactions occurring during the process is still very far indeed from complete, so that it is only possible as yet to discuss these changes in very broad outline.

In considering these reactions it is most convenient to deal first only with the carbon and hydrogen, these being the most important constituents from a gas-making point of view. When heated above its decomposition-point in closed vessels, coal, like almost all organic substances, is resolved into two portions: (1) a solid, non-volatile portion; and (2) a volatile portion, partly liquid and partly gaseous at the ordinary temperature. It is an invariable rule that the volatile portion, as a whole, contains a higher proportion of hydrogen and lower proportion of carbon than the original coal, whilst the reverse is the case with the non-volatile portion. When the temperature employed is the lowest at which any substantial decomposition occurs, namely, 300°–400°, a very large proportion of the volatile products consists of substances which are liquid at the ordinary temperature, and only a small yield of gaseous products is obtained, the latter consisting chiefly of methane, ethane, and ethylene, with smaller amounts of their higher gaseous homologues, and only a low percentage of hydrogen. The liquid products consist chiefly of hydrocarbons of the paraffin and olefine series, with smaller amounts of members of the acetylene series, or of their derivatives, *i.e.* of substances relatively rich in hydrogen.

The residue obtained at such a temperature still contains a fair percentage of hydrogen, and burns in the air with production of flame, but not of smoke. Where the chief product desired is a residue of this kind still containing hydrogen, such as the material sold now under the name of 'Coalite,' or where, as in the Scotch shale-oil industry, a tar containing paraffin and olefine hydrocarbons is the product of greatest value, such low temperature carbonisation may be advantageous. The yield of gas under these conditions is, however, so small (although of high calorific and illuminating power) that the employment of such temperatures is not practicable commercially as a general rule, where the gas is the primary product required, and for such purposes higher temperatures must be employed.

When the closed vessel is heated more strongly, the coal placed into it only rises in temperature gradually, and, therefore, at first undergoes the above low-temperature decomposition. The further action of heat then brings about fresh changes, both in the above hydrogen-containing residue and in the volatile substances primarily evolved from the coal. The effect of further heat on the residue is to drive off more hydrogen, which, at temperatures of 700°–800° is mostly evolved as methane and free hydrogen, the latter being present in larger proportion, the amount of other gaseous hydrocarbons being very much smaller than in the gas produced at low temperature. The residual coke becomes denser and harder, but at this temperature still contains hydrogen in appreciable quantity, and on raising the temperature to the highest obtainable in practice, an additional yield of gas is procured still consisting of methane and hydrogen, but as the temperature increases the percentage of methane falls and that of hydrogen rises. The higher the temperature to which the residual coke is finally heated, the greater is therefore the yield of combustible gas.

The volatile products first evolved from the coal, consisting chiefly of compounds which are liquid at the ordinary temperature, also undergo further change when a higher carbonising temperature is employed, if they are subjected to the action of this heat before they can escape, yielding a large proportion of gases which are permanent at the ordinary temperature, the most important of these being hydrogen, methane, ethylene, and benzene. The latter, although a liquid at the ordinary temperature, is so volatile that most of it remains in the gas.

On the other hand, simultaneously with the

formation of these gases, the petroleum-like products yield many substances which contain a higher percentage of carbon and a lower percentage of hydrogen than is present in the substances from which they are formed, consisting of hydrocarbons of the aromatic series, such as benzene, naphthalene, anthracene, and their derivatives. These are liquids at the ordinary temperature, or, if solid (like naphthalene and anthracene), are soluble in the other liquids and condense together as a fairly fluid tar in the subsequent cooling of the gas. By heating the primary volatile products to a moderate temperature, therefore, the yield of permanent gas is largely increased, and that of the tar diminished, and the latter now consists chiefly of aromatic, instead of fatty, organic derivatives; making the tar of especial value for the coal-tar colour industry.

If the volatile products are subjected for any length of time to still higher temperatures before escaping, such as a bright red or white heat, further decompositions take place, which, on the whole, are by no means favourable to the production of gas. The tar vapours of the aromatic series undergo further decomposition into still denser hydrocarbons, and a gas consisting mainly of hydrogen; and many of the new hydrocarbons formed are solid even at a red heat, and are quite insoluble in the remaining liquid tar. These are partly deposited on the heated retort walls as 'carbon' or 'scurf,' and are partly carried away with the hot gas as finely divided particles, and are carried down during cooling with the tar, making this much more viscous even when hot. Further, even the gaseous compounds undergo further decomposition; the benzene undergoing partial conversion into hydrogen and denser hydrocarbons, the ethylene yielding some hydrogen and methane, as well as tarry matter, and even the more stable methane undergoes a partial decomposition into its elements hydrogen and carbon.

The chemical considerations therefore lead to the conclusion that while in order to obtain the maximum yield of gas from coal it is advisable to subject the latter finally to as high a temperature as possible, so as to drive off the volatile matter completely, the gases and vapours produced in the distillation should only be subjected to a considerably lower temperature than that to which the coke is eventually heated, as too high a temperature results in the separation of carbon, which would otherwise have remained as gaseous hydrocarbons in the gas; thus depreciating both its calorific and illuminating power. On the other hand, it is equally evident that these volatile products must not be subjected to too low a temperature, for in that case the hydrocarbons, &c., produced in the early stages of distillation would not be sufficiently decomposed, and would be lost from a gas-making standpoint—being condensed in the tar.

The remaining constituents of the coal concerned in the production of gas are oxygen, nitrogen, and sulphur. The ash remains in the coke, and need not be further considered here. Oxygen is present in considerable amount in the coal substance; and the coal as used also always contains either moisture in the free state or in such a loose state of combination that it is given off at temperatures below 100°—the amount varying usually from 1 to 4 p.c. The oxygen in the coal substance is probably evolved in the early stages to a considerable extent as steam and volatile compounds of carbon, hydrogen, and oxygen; and the latter, on further heating, are largely decomposed, forming steam, carbon monoxide, and carbon dioxide. As the temperature rises, the carbon dioxide tends to combine more and more with the red-hot carbon present, undergoing reduction to carbon monoxide, and the steam tends also to act on the carbon, with production of water gas; and the higher the temperature to which the gases are heated, especially while in contact with the coke, the greater is the amount of carbon monoxide formed, and the higher also the amount of steam converted into water gas. Some of the oxygen is found in the tar as compounds with carbon and hydrogen, such as phenol; but the bulk of it remains as steam, which condenses out on cooling, and, roughly, about one-fourth is found in the gas as oxides of carbon.

The effect on the nitrogen is similar to that on the hydrogen. At very low temperatures some ammonia is given off, and also substances containing carbon, hydrogen, and nitrogen, which condense in the tar; while a large proportion of the nitrogen remains in the residue. At higher, but still moderate, temperatures, much more nitrogen is given off from the coal, and the above volatile products are largely broken up, with the formation of ammonia and some free nitrogen; and at such temperatures the maximum yield of ammonia is obtained. At still higher temperatures, more nitrogen is evolved from the coke; but the ammonia itself is then largely decomposed into its elements nitrogen and hydrogen, and also reacts with the hot carbon, producing hydrocyanic acid; and, in spite of the more complete elimination of the nitrogen from the coke, the yield of ammonia is decreased. Only from 14 to 17 p.c. of the nitrogen in the coal is recovered in the form of ammonia (*v.* AMMONIA). Some of the nitrogen is also found in the tar, chiefly in the form of nitrogenous bases, such as pyridine.

The sulphur, too, probably comes off first as compounds with carbon, and hydrogen; and these, when more strongly heated, yield sulphuretted hydrogen, which can be removed from the gas without much difficulty. At still higher temperatures, however, the decomposition of these volatile organic sulphur compounds takes place, with formation of larger quantities of carbon disulphide; this compound being also produced, but probably in much smaller amount, in the gases last driven off from the coke, due to the sulphur still remaining in the latter. High temperatures, especially if allowed to act fully on the volatile products, therefore tend to increase considerably the amount of this impurity, which can only be removed with difficulty.

Both with regard to sulphur and nitrogen, therefore, as well as in the case of the hydrocarbons, it is desirable that the volatile products themselves shall only be heated to a moderate temperature if a maximum yield of the valuable product (ammonia) and a minimum yield of the deleterious impurity (carbon disulphide) is to be obtained. In the case of the oxygen compounds alone does there appear to be any

advantage in subjecting these products to a high temperature, owing to the larger proportion of carbon monoxide and smaller proportion of carbon dioxide produced, as well as to the larger amount of steam converted into combustible gas. On the whole, the advantages gained in the latter respect are more than counterbalanced by the deleterious action of such high temperatures so far as the hydrocarbons and the nitrogen and sulphur compounds are concerned.

In addition to the changes brought about by thermal decomposition, which are the most important, formation of other compounds also occurs by polymerisation or synthesis from two or more of the products of thermal decomposition, such as the formation of benzene and stilbene by condensation of acetylene, and a large number of the tar constituents are doubtless formed in this manner. So far as the gaseous products are concerned, the formation of carbon monoxide by the action of the dioxide on carbon, and the synthesis of water gas by the interaction of steam and carbon, have been referred to. In addition, there is some evidence that methane may also be formed to some extent in the carbonising process by synthesis from hydrogen and carbon monoxide, in accordance with the reversible reaction $CO+3H_2 \rightleftharpoons CH_4+H_2O$. This reaction occurs almost quantitatively when a mixture of the gases is passed over metallic nickel at 250° (Sabatier and Senderens, Compt. rend. 134, 514), and although, as the temperature rises, the reverse reaction takes place in increasing degree, the evidence available points to the conclusion that appreciable amounts of methane are formed in this manner under some conditions during carbonisation.

In the carbonisation of coal in the most usual gas-works practice, the coal, as above described, is placed in a long narrow retort set either horizontally or at an angle of about 32° to the horizontal, leaving a considerable amount of free space above the coal through which the evolved gas must pass to reach the exit pipe at one or both ends of the retort. The carbonisation commences on the outside of the mass—namely, at the bottom and sides—where it is in contact with the heated retort wall, and also at the top, where it is affected by the heat radiated through the free space from the hot crown of the retort. The coal on the outside first becomes pasty and agglomerates, and then undergoes the low-temperature decomposition already described, the resultant vapours and rich gas escaping fairly readily into the free space above the coal. Here they are subjected to the further action of heat in two ways—namely, by contact with the heated walls of the retorts, and also by the action of the radiant heat rays which are traversing the free space. The net result of their combined action is to raise the temperature of the vapours passing through the free space, and to bring about much change; and the higher the temperature to which the retort walls are heated, the greater is the amount of further decomposition that they undergo.

The further action of heat on the pasty mass on the outside of the charge converts this eventually into coke; heat passing simultaneously further into the charge and converting the layer below into the pasty condition, which is assisted by the condensation on these lower layers of some of the tarry matters formed by the decomposition of the hotter layers above, and the extent to which such condensation occurs doubtless has much influence on the physical properties of the resulting coke. This sequence of changes continues until the heat has penetrated to the centre of the mass, and effected its complete carbonisation. After the first layer of hot coke has been formed, the gases produced from the interior of the charge, in order to escape from the retort, must not only undergo the ordeal of heat in passing through the free space, but also pass through the hot layer of coke on the outside of the charge; and the temperature and area of this coke mass constantly increases as time goes on. Further, as carbonisation proceeds, the rate at which the gas is evolved decreases, and in consequence, its speed through the free space becomes less, and it is exposed to heat there for a greater length of time. From all these causes, the quality of the gas falls off after the first hour, and especially when the carbonisation is approaching completion. The percentages of methane, ethylene, benzene, sulphuretted hydrogen, and carbon dioxide steadily diminish as time progresses, and that of hydrogen steadily increases; while that of carbon monoxide varies less considerably, as shown by the following table, giving the analysis of the gas evolved at different stages from a retort charged with Derbyshire coal, the temperature of carbonisation being about 950° :—

	Hours after commencement				
	½ hour	1½ hrs.	2½ hrs.	3½ hrs.	5 hrs.
Sulphuretted hydrogen .	3·8	3·1	2·8	2·1	1·2
Carbon dioxide .	3·0	2·8	2·6	2·3	1·7
Ethylene and benzene .	8·6	5·2	3·6	2·4	0·0
Oxygen . .	0·0	0·0	0·0	0·0	trace
Carbon monoxide	4·4	5·0	4·9	4·5	3·8
Methane . .	49·7	42·0	39·4	37·5	26·3
Hydrogen .	29 8	37·5	42·2	46·2	60·8
Nitrogen (by diff.)	0·7	4·4	4·5	5·0	6·2

Before the introduction of gaseous firing, the retort temperatures obtained in practice did not usually exceed about 900°C., or 1650°F. Under these conditions, the volatile products were not materially overheated, and gas of high illuminating power was produced; while the tar simultaneously formed was fairly fluid, and only contained moderate amounts of the objectionable 'free carbon.' The quantity of naphthalene formed was also not excessive, and that of 'light oils' simultaneously produced was, in most cases, sufficient to wash the naphthalene out of the gas during condensation to a sufficient extent to prevent its subsequent deposition in the solid state in the mains and services. On the other hand, under these conditions, a relatively low yield of gas per ton is obtained, as an appreciable quantity of volatile matter is left in the coke.

When, with the aid of gaseous firing, higher carbonisation temperatures were employed,

matters were considerably modified, as the volatile matter of the coal was more completely evolved with the production of a greater volume of gas. But, as we have seen, it follows inevitably that, in a horizontal or inclined retort having a large free space above the coal, the volatile products must also be more strongly heated by an increase in the retort temperature; and, as a result, under these conditions, the gases and vapours undergo a more far-reaching decomposition than before, and a reduction in the quality of the gas is brought about. Some of the hydrocarbons formerly present in the gas are now deposited in solid or liquid form, which either remain in the retort as carbon or are condensed with the tar, and are lost from a gas-making point of view. Simultaneously, other disadvantageous changes occur, inasmuch as the tar produced is thicker and contains much more 'free carbon,' thereby increasing the trouble from stopped ascension pipes and pitched hydraulic mains, and greatly increasing the practical difficulties of retort-house working. Further, the action of these high temperatures on the volatile products increases the production of naphthalene and decreases that of light oils, and renders the cooled gas much more liable to deposit solid naphthalene in the mains and services both on the works and in the district, causing serious trouble both to supplier and consumer.

In spite of these last-named drawbacks, the employment of higher temperatures has, on the whole, proved favourable; the increased yield obtained from the more complete elimination of the volatile matter of the coal having more than counterbalanced these disadvantages. Nevertheless, a process of carbonisation is very desirable, in which the coal itself can be heated to a high temperature without simultaneously causing too great heating of the volatile products; and it is largely with a view to this end that modifications of the method of working have been introduced during the past few years.

From what has been said, it is clear that one of the chief causes of the overheating of the gases and vapours is the existence of a large free space above the coal in the retort. With the horizontal retort, so long as the coke had to be extracted by a rake, worked either by hand or mechanically, a considerable amount of free space was necessary in order to afford room for the introduction of the rake-head above the coke; but the invention of mechanically propelled pushers, which discharge the coke by pushing from one end of the retort, has done away with the necessity of the free space for the removal of the coke, and has made it possible to put in a much larger charge of coal without increasing the difficulties of discharging the latter. In recent years, therefore, by the introduction of such increased charges, the amount of free space has, in many works, been largely reduced in horizontal retorts, so that the gases and vapours are exposed to a smaller amount of retort surface, and, still more important, owing to the volume of the free space being smaller, they pass through it more quickly, and are exposed to the action of the heat for a shorter time. As the practical result, it is found that the coke produced is larger, a thinner tar containing less free carbon is produced, owing to the lessened overheating, less carbon disulphide is produced, less trouble from naphthalene ensues, and retort-house working is considerably facilitated. Whether the total heat value of the gas obtained from a ton of coal—*i.e.* the multiple of gas per ton × calorific power—is greater than can be obtained with the smaller charges, is a matter on which different opinions prevail at present.

On the other hand, owing to the increased thickness of the charge, a longer period must be allowed for its carbonisation if the central core is to be completely carbonised; and beyond a certain weight of charge, varying apparently with different classes of coal, the gas production per retort per 24 hours falls off, or can only be maintained by increasing the carbonisation temperature above that employed with the smaller charges. Such higher temperatures also increase the heat to which the gases are exposed in the free space; but experience seems to show that the effect of such increase is small when the volume of free space is low, or, in other words, that in bringing about decomposition of the volatile products the time during which the gas is exposed to heat is much more important than the temperature of the retort walls.

Carbonisation in vertical retorts. But, while the amount of free space can be in this manner greatly reduced, it is scarcely practicable to eliminate it altogether in horizontal retorts. If, however, the retort is placed in a vertical instead of a horizontal position, this is readily effected; as, in the nature of things, the coal when charged in from the top must completely fill the retort. Although a small amount of free space may be left at the top, matters can be so arranged that this is not too large and that the retort walls at this point are not heated to any great extent. Hence latterly carbonisation in vertical retorts has been much investigated, and is now practised in a large number of works.

Intermittent vertical retorts. In the Dessau vertical retort system, patented by Bueb (Eng. Pat. 1393, 1904), the previous practice is adhered to, in so far that the coal is charged into the retort from an overhead hopper all at once, and allowed to remain there until carbonisation is complete, when the coke is discharged by gravity and the retort refilled with fresh coal. The retorts are either 4 or 5 metres in length, having an oblong cross section with rounded corners and are tapered, increasing in size from top to bottom to facilitate the discharge of the coke. Until recently 10 or 12 retorts were set in rows of two in a setting, each setting being heated by gas from a separate deep producer capable of being filled much above the point at which the producer gases are drawn off, so that it may run for 24 hours without recharging. Fig. 10 gives a vertical section of such a setting and producer, showing clearly the general arrangement of the plant.

As the thickness of the charge is greatest at the bottom, the highest temperature is maintained at this point, with a rather lower temperature in the upper portions where the thickness of the charge is less. The result of this arrangement is that, even at high temperatures, not only is a large yield of gas obtained, but at the same time the tar formed is very fluid, and only contains a small percentage of free carbon.

Simultaneously, the naphthalene production is lessened, and that of the lower boiling tar constituents increased, with the result that the naphthalene is sufficiently completely removed from the gas in the ordinary process of condensation, without the adoption of any special treatment, and, at the same time, the amount of sulphur obtained in the form of carbon

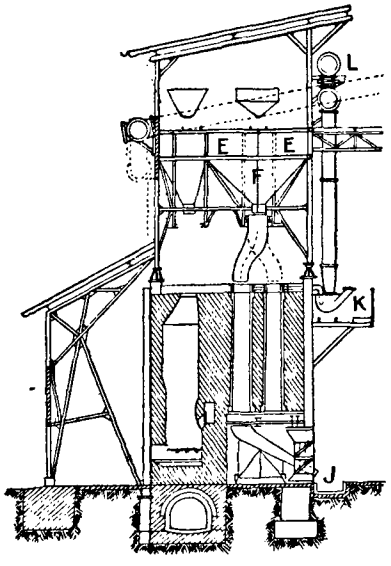


FIG. 10.

disulphide is reduced. The yield of ammonia is also said to be materially higher, and the coke produced is harder and denser than that formed from the same coal in horizontal retorts.

In spite, therefore, of very high retort temperatures, the objectionable overheating which occurs with horizontal retorts having a highly heated free space above the coal, is obviated in such vertical retorts. This is largely due to abolition of this free space, but other conditions also come into play. In the horizontal retorts, after a layer of incandescent coke has been formed on the exterior of the charge, all gas produced from the unaltered coal in the centre of the charge must find its way out through the incandescent layer, and thus be subjected to considerable heat. In the intermittent vertical retort, the carbonisation also takes place from the periphery inwards, and a layer of incandescent coke is formed in the early stages, but in this case the gas produced from the still uncarbonised coal in the centre of the charge has two possible paths of escape—on the one hand, through the hot coke layer, and on the other, through the cool central core of uncarbonised or partly carbonised coal, and the gas travelling in the latter direction escapes overheating by the hot coke layer. The relative amounts of the gas which travel in each direction is still a matter in dispute, but Bueb holds the view that the great bulk of the gas travels through the cool central core.

The period required for complete carbonisation varies usually from 10 to 12 hours, and during the last 1 or 2 hours steam is frequently admitted at the bottom of the retort with production of water gas, which mixes with and dilutes the coal gas produced. This dilution causes a considerable decrease in the illuminating power of the mixed gas produced, but effects a much smaller proportional reduction in the calorific power, and this procedure is extensively adopted, especially in Germany, where very many installations of the Dessau retorts are at work, as in that country no attention whatever is now paid to illuminating power, only the calorific power being considered.

In the latest form of the Dessau retorts, the length of the oblong cross section has been reduced, and these retorts set in rows of three, which are charged and discharged simultaneously. The reduction in the size of the retort increases the proportion of heating surface to the cubic capacity of the retort, and results in a more rapid carbonisation and increased output of gas, and also a reduced fuel consumption.

Continuous vertical retorts. In this system of carbonisation, the object aimed at is not only to avoid an excessive heated free space above the coal, but also to render the process a continuous one, by the addition of mechanical arrangements whereby the coke is withdrawn continuously, or nearly so, from the bottom of the retort, fresh coal being added to the retort at the top to replace the coke withdrawn, so that the coal to be carbonised slowly travels down the retort, undergoing gradual conversion into coke and gas. The conditions in the retort, therefore, remain approximately constant, and the quantity and quality of the gas evolved remains fairly constant, instead of both falling off as carbonisation proceeds, as is the case with an intermittently charged retort.

The continuous system of carbonisation has been chiefly worked out in this country. Although many experiments in this direction were made in the last century, none met with any degree of success. In the early years of the present century, however, very interesting results were obtained with the Settle-Padfield continuous vertical retort (Eng. Pat. 12552, 1902; 24588, 1903), which showed that excellent carbonising results, so far as yield and quality of gas and coke were concerned, could be obtained in this manner, although, largely owing to difficulties arising from the shape of retort adopted, the practical difficulties found in working it have prevented its further adoption. At the present time two such continuous processes, namely, the Woodall-Duckham system (Eng. Pat. 16497, 1903; 15053, 1907) and the Glover-West system (Eng. Pat. 23650, 1905; 2663, 1907; 7534, 1907; 8572, 1909), are in use, a diagrammatic section of each of these plants being shown in Figs. 11 and 12, from which the general arrangement is readily seen. In the Woodall-Duckham retorts, the discharge of the coke is controlled by the coke-feed roll shown below the retort, which is slowly revolving, and as it rotates allows the coke to fall into the chamber below, from which it is emptied periodically, the speed of the coal through the retort being regulated by varying that of the feed roll. As the coke is removed, the whole mass in the retort falls, leaving a space at the

top, which is at once filled by fresh coal introduced by a rotating feeding device fixed at that point. The retorts, four of which are placed in a setting, are 25 feet in length, and have a considerable taper to facilitate the downward movement of the mass. The heating is effected by producer gas, which, with the secondary air,

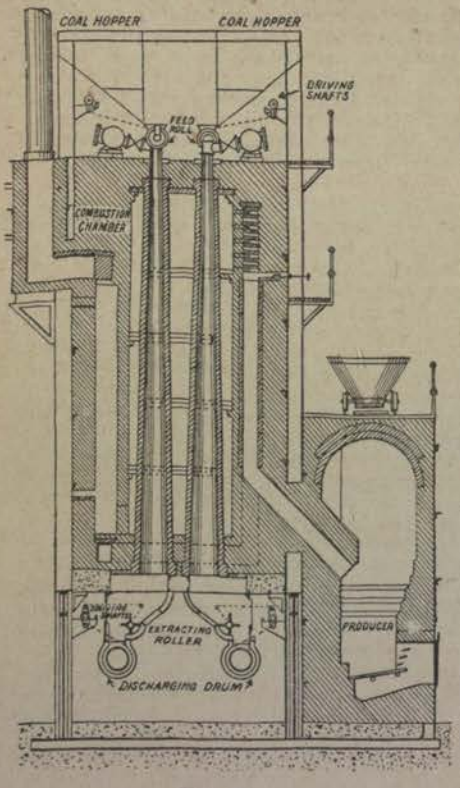


FIG. 11.

enters at the top, the mixed gases passing downwards, the temperature on the outside of the retorts being highest at the top and decreasing to the bottom of the retorts.

In the Glover-West system, the discharge of the coke is effected in a somewhat different manner. In the diagram shown, the coke issuing from the bottom of the retort rests on a horizontal plate fixed about 8 inches below the bottom, and is gradually swept over the edges of the plate by a radial arm, which is slowly revolving in a horizontal plane just above the plate, this arm being mechanically actuated from the outside, the speed at which it is worked controlling the rate of carbonisation. The coke falls into the chamber below, and is removed at intervals. As the mass moves downwards, leaving a space at the top, the latter is at once filled by coal falling in by gravity from a small hopper above each retort, closed by a gas-tight valve at the top, shutting it off from the main coal bunker above, this small hopper being charged every few hours by opening the valve and allowing it to fill up from the main bunker. In more recent plants the above resting plate and radial arm are replaced by a slowly rotating screw conveyor, which effects the gradual discharge of the coke. The retorts are from 20 to 23 feet in length, and tapered, eight being placed in a single setting. For the purposes of heating, the setting is divided into a number of sections by horizontal division walls, the three upper sections receiving the combined waste gases from the chambers below, and abstracting much heat from these before they pass to the chimney. The next six sections form the heating chambers proper, each receiving a separate supply of producer gas from the furnace, as well as a separate supply of secondary air, and by suitably regulating the supplies, the temperatures in the different sections can be adjusted to that found most suitable for the particular coals carbonised. In the lowest section, the secondary air is admitted on its way to the heating sections, and thereby cools the

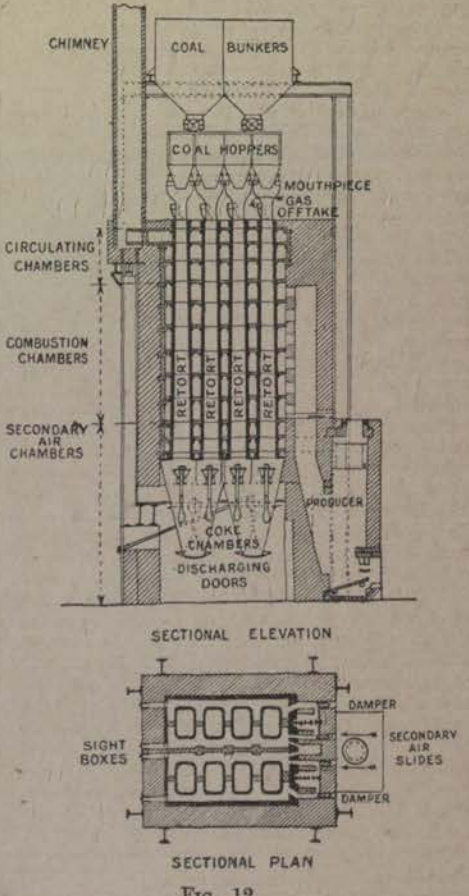


FIG. 12.

now carbonised coke passing through the retorts, so that this is discharged in a relatively cool condition, and requires no quenching, its heat being returned to the setting with the secondary air, effecting a considerable economy in the fuel consumption.

The constant movement of the mass through

the retort in such continuous vertical retorts modifies the conditions of carbonisation to some extent. As with the intermittent retorts, the heat penetrates the mass of coal from the periphery and travels inwards, but as the coal is constantly moving downwards, the uncarbonised coal takes the form of an inverted cone, the base of which is at the top, and the apex at a point about two-thirds of the length of the retort below. A small proportion of gas, with much steam, is formed on the inner and cooler side of the layer of decomposing coal, and escapes up through the core of uncarbonised coal, but the bulk of the gas is formed on the hotter outer portion of the decomposing layer and passes up through the surrounding hot coke. Only a limited amount of free space is left at the top. The tar produced is thin and contains but little free carbon, no naphthalene trouble occurs with the gas after condensation, the carbon disulphide is reduced, and at the same time a high yield of gas of good calorific power is obtained. The coke formed from the continuous process is usually less dense than that obtained by intermittent carbonisation in vertical retorts.

Carbonisation in larger bulk. Considerable attention has recently been paid, especially in Germany, to the carbonisation of coal for gas-making purposes in much larger bulk than the gas retort, and more in accordance with the practice where metallurgical coke is the product primarily required (*see* art. COKE). In this industry, as the gas is a by-product, the latter is employed for heating the ovens, but as with good working only about half the gas made is required for this purpose, a considerable surplus remains, which is generally used for boiler firing or in gas engines. In several instances in this country, however, a portion of this surplus gas, enriched, if necessary, with benzene to give it sufficient illuminating power, is employed for public distribution in the neighbourhood of the coke ovens, and in 1911 an installation for the supply of a considerable district from the Brackley coke ovens in Lancashire was started. In the Westphalian coal-fields, the surplus gas from a large number of ovens is now being collected and distributed over a very wide area.

In the coke-oven industry, the object aimed at is not only the production of coke, but also the utilisation of the slack inevitably produced in the operation of mining. This is first washed to remove mineral impurities as far as possible, and, when charged into the ovens, lies in a dense mass, which may be 10 tons or more in weight, and has very small interstitial spaces, and is sometimes further specially compressed; moreover, it contains 10 p.c. or more of moisture. Whilst the result of these alterations in the conditions from those in gas retorts effects an improvement in the quality of the coke produced, the gas, as it is formed, has greater difficulty in escaping from the centre of the charge, and the volume produced is usually lower, although it is of good calorific power, provided due precautions are taken to prevent the drawing in of undue amounts of furnace gases or air. The rate of carbonisation is also naturally much slower, as the larger the bulk in which the coal is charged the smaller is the *ratio* of heating surface per unit weight of coal, which further influences, to some extent, the composition of the resulting gas.

In Germany, particularly during the past few years, extensive experiments have been made with carbonising chambers of rather smaller size than coke ovens, holding from 3 to 6 tons per charge, in which the heating is effected by producer gas manufactured from the coke, and ordinary gas coal is carbonised instead of washed slack. In some of the forms adopted, horizontal chambers are used, and in others, these are provided with a sloping bottom, to facilitate the charging of the coal and discharge of the coke (*see* J. Gas Lighting, 1909, 106, 832). The coke obtained with such chambers is more closely allied to metallurgical coke than to ordinary gas coke, but where ordinary gas coal is used, the results, so far as quality of gas, tar, and ammonia are concerned, do not appear to differ materially from those obtained with vertical retorts. The relative advantages of such chambers and retorts lie more in connection with questions of the capital and working costs, of the desirability of such large carbonising units for making a uniform quality of gas, for adjusting the gas output to the seasonal variation in the demand for a public supply of gas, and of the suitability of the quality of coke produced to supply the local demand. Since 1911 very few installations of this intermediate type of chambers, between the size of retorts and coke ovens, have been adopted in this country.

CONDENSATION OF THE HOT GAS.

The volatile products driven off from the coal issue from the retorts into the mouthpiece, at a high temperature, which may, at times, reach 700°–800°, but this falls very rapidly as the gas passes up the ascension pipe. This arises partly from the fact that the difference in temperature between the gas within and the air circulating around the pipe is very great, and partly because the number of heat units to be removed for a given temperature interval is relatively small, being due to the specific heat of the gases, and the latent heat of the tar vapours which condense, both of which are comparatively low. The temperature, therefore, falls rapidly up to the point at which water commences to condense, which is usually about 75°–80°, and from this point onwards the rate of cooling becomes very slow, chiefly owing to the high latent heat of the steam present. The dew-point is mostly attained by the time the gas reaches the dip pipe, and the temperature of the gas in the hydraulic or dry main, where the streams of gas from the different retorts mix, averages about 60°. By the time the steam commences to condense, by far the greater part of the tar vapours present have liquefied, and, owing to the rapid rate of cooling, these separate in the form of finely divided drops or vesicles, which are carried along with the stream of uncondensed gas mechanically in the form of a dense brown fog. In passing through the hydraulic or dry main, the greater part of this fog (generally from 70 to 80 p.c.) coalesces to form liquid tar, a considerable amount of water also separating here also, which combines with the ammonia and other impurities of the gas, forming ammoniacal liquor, these two liquids

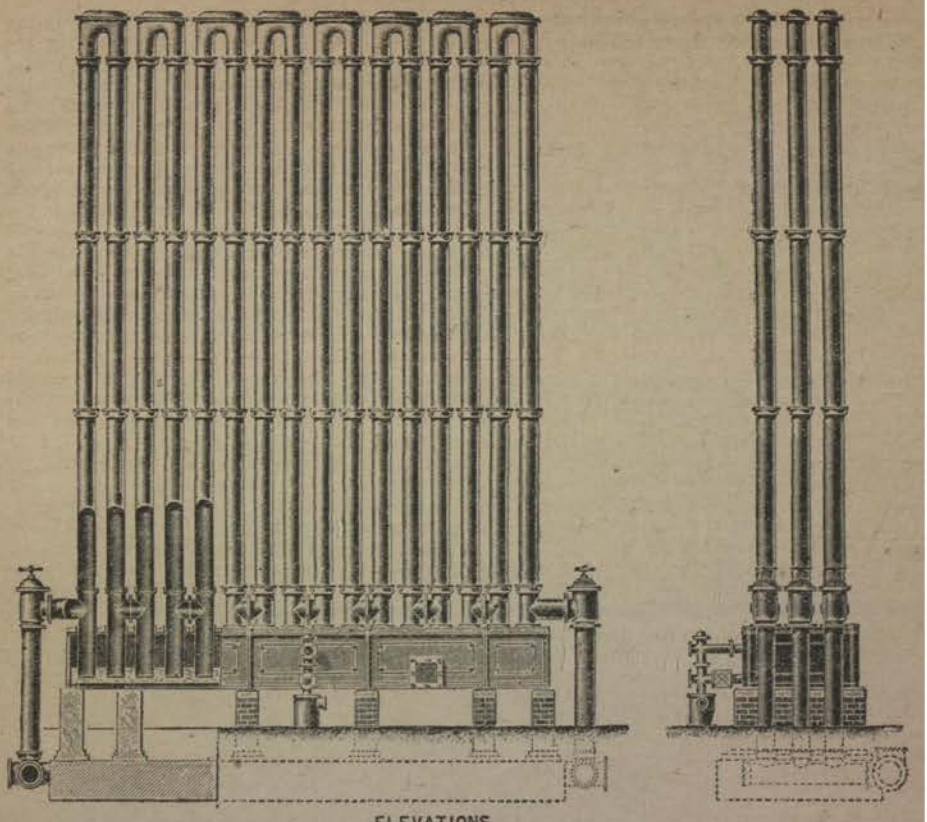


Fig. 13.

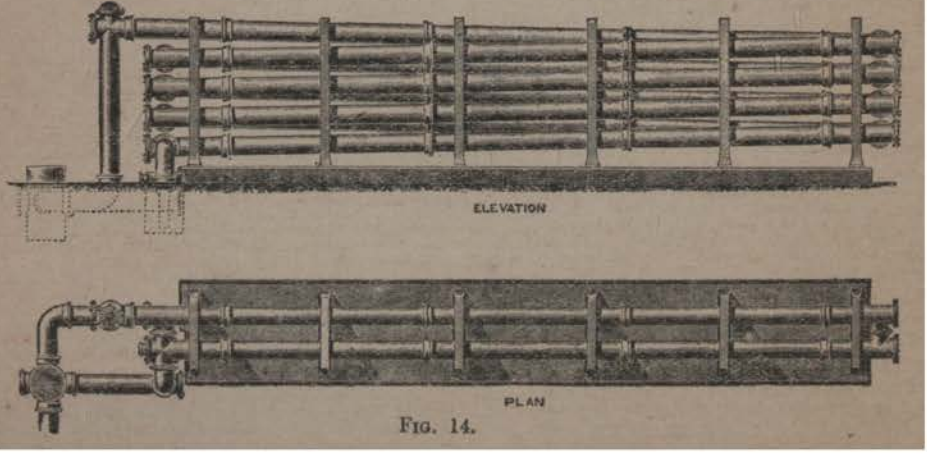


Fig. 14.

being removed in the manner already described. The combined streams from all the collecting mains of the separate setting unite in a trunk main termed the 'foul' main, by which they

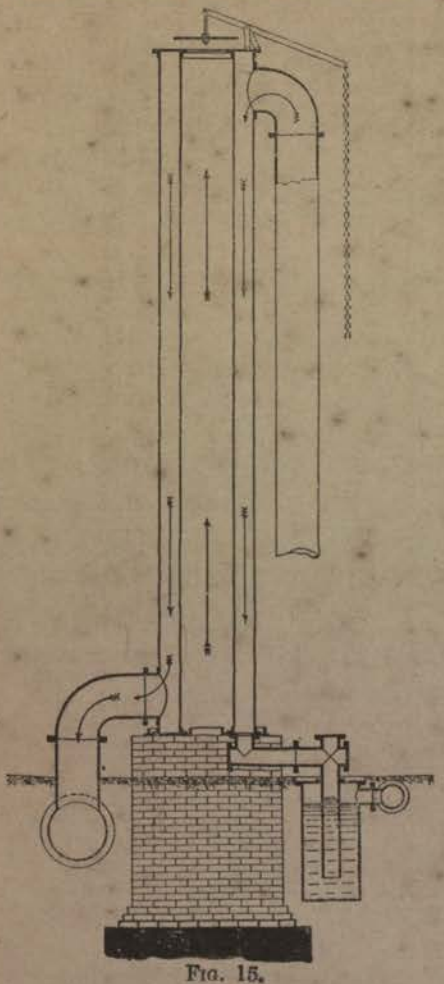


FIG. 15.

are conveyed from the retort house to the condensing plant proper, the combined stream having at this point a temperature of 50°–60°, and still containing much suspended tar fog, amounting in some cases to as much as one-third of the total tar production.

The cooling of the gases to approximately atmospheric temperature is effected by means of either atmospheric condensers or water-cooled condensers. Although many types of the former, differing in external appearance, are in use, the arrangement is in all cases such that the gas is passed slowly through apparatus exposing a large surface to the air, whereby the sensible heat of the gases and the latent heat of the vapours is given up to the air passing over the surface. In the water-cooled condensers water is employed as the cooling medium in place of air. This type of condenser requires a much smaller cooling surface than the atmospheric type, and the temperature to which the gas is cooled can be more readily regulated by controlling the flow of water, provided a sufficient supply of cold water is always available.

Fig. 13 shows the general arrangement of a vertical, and Fig. 14 of a horizontal, atmospheric pipe condenser, the manner of working being readily apparent from the diagram. Fig. 15 gives one section of an annular atmospheric condenser, in which the gas passes through the annular space between the inner and outer pipes, the air circulating not only over the outer pipe, but also ascending up the inner pipe, cooling both surfaces of the annular chambers. The volume of air passing up the inner pipe can be varied by means of the damper shown, and the extent of cooling of the gas regulated to some extent in this way. Fig. 16 gives a vertical and cross section of a water-cooled tubular condenser, the gas passing downwards over the

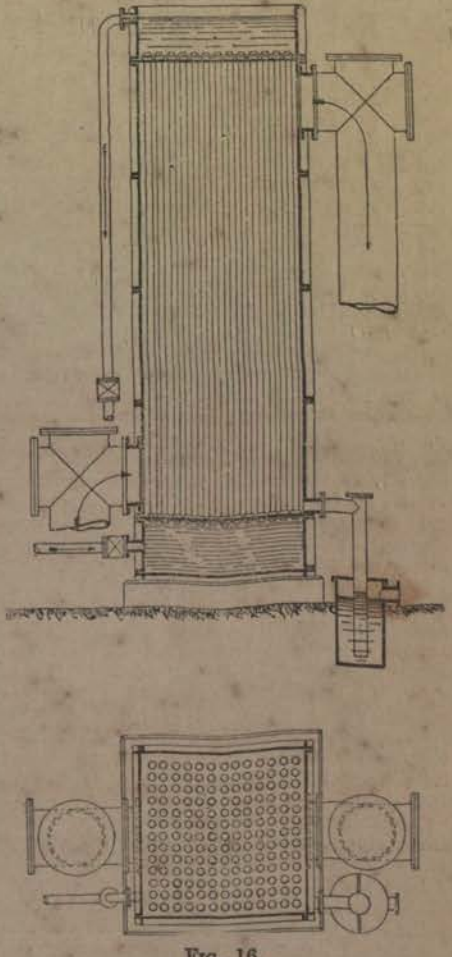


FIG. 16.

outer surface of the small pipes, the water travelling up the pipes in the reverse direction to the gas stream, so that the gas leaving the apparatus is finally cooled by the incoming cold

water. Many other good forms of both atmospheric and water condensers are in use, but their action is, in general, similar to those described.

When high carbonising temperatures are employed, especially with certain classes of coal, the tar separating in the cold end of the condenser is apt to become semi-solid from crystallisation of naphthalene, eventually causing a stoppage. To avoid this it is convenient to arrange the connections and valves in such a manner that the inlet and outlet can be reversed; the previously cold end then receives the hot gas, and the thick tar becomes fluid and flows to the tar well, so that by periodic reversals of the stream blocks from this cause can be largely avoided.

In this country, where the seasonal changes in temperature are not, as a rule, very extreme, atmospheric condensers are employed to the largest extent, water condensers being employed frequently in addition to effect the final cooling of the gas. On the Continent, where lower temperatures often prevail in winter and higher in summer, water condensers are more frequently used, and are enclosed in buildings to protect them from extremes of temperature.

In the early days of the manufacture, the only point considered was the simple cooling of the gas, but it was soon found that the manner in which the cooling takes place and the temperature to which the condensed tar is cooled in contact with the gas has a very material effect on the illuminating power of the gas produced. This arises from the fact that the illuminating power of the gas is very largely dependent upon the amount of benzene vapour present in it, and the lower the temperature to which the tar is cooled when in contact with the gas, the greater is the proportion of the benzene retained by the tar and the lower that left in the gas. The object at present aimed at in condensation is, therefore, not merely to cool the gas, but to carry out the cooling in such a manner as to leave in it the maximum amount of benzene vapour that it can retain at the lowest temperature to which it may be subsequently exposed during distribution, and, at the same time, to remove as completely as possible the vapours of higher-boiling substances, especially naphthalene. The importance of the removal of the latter arises from the fact that it is a solid at the ordinary temperature, and, when present, is liable to be deposited in crystals as the gas cools, and then causes blocks in the subsequent manufacturing plant and in the distribution system, causing great inconvenience. Although the amount of naphthalene in the gas sent out from the works rarely exceeds 15–20 grains per 100 cb. ft., and is usually less, the deposited naphthalene may, when weather conditions are favourable to its separation, cause the stoppage of hundreds of service pipes in a single night in a large town.

To effect the maximum retention of the lowest boiling-tar constituent, benzene, and the most complete removal of the higher-boiling constituents, the ideal procedure would be to arrange the condensing system so that the whole of the products of condensation flowed back in the opposite direction to the gas, whereby the gas is continually exposed to the solvent action of the liquids condensed from it at a lower temperature, in exactly the same manner as the vapours from a mixture of liquids are treated in a fractionating column in the process of fractional distillation. This principle is, however, very difficult of application in its entirety in the coal-gas manufacture, for many reasons. In the first place, as already mentioned, the separate streams from each retort undergo such rapid cooling before they combine to a single stream, that the tar has largely separated as a fog, which is inevitably largely carried forward mechanically with the gas, instead of travelling in the reverse direction; and, secondly, water also condenses from the gas, and as this does not mix with, and is specifically lighter than, the tar, it tends to cover the surface of the separated tar, and prevent the latter exerting its full solvent action on the substances still present as vapours in the gas. Where the coal is carbonised in larger units, as in coke ovens, the combined streams from the different ovens have a much higher temperature: here a strictly counter-current process is more possible, and Feld has patented a process for the treatment of such gas in a series of mechanical washers, in which the gas is successively washed with the products condensing at a lower temperature, the tar being obtained direct from these in different fractions, corresponding to those obtained in the first distillation of coal tar, and free from water, as the temperature is not allowed to fall to the point at which steam commences to condense (Eng. Pat. 26262, 1905; 20139, 1907; 27567–8, 1907; 9086, 1910). The process is being tried at the present time in coke ovens abroad. The removal of tar fog from the hot gas from coke ovens at temperatures above the dew-point is also carried out by the Otto process (*see* art. COKE).

The adoption of the counter-current system in gas works in the later stages of condensation, tends to have a beneficial effect, but the extent is only slight, owing to the above-mentioned protective effect of the condensed ammoniacal liquor, the quantity of which is much greater than that of the tar after the gas leaves the hydraulic main. In general, the widest divergence occurs in practice as to the manner in which the condensed tar is allowed to flow, this being sometimes with and sometimes against the gas streams, and sometimes alternately in each direction. It is, however, generally agreed that the tar which separates at the earliest stages, namely, in the hydraulic main, should be removed from contact with the gas before the temperature of the latter is reduced below 30°–35°, as otherwise considerable reduction of illuminating power occurs, owing to absorption of benzene vapour from the gas.

Formerly, when gas of higher illuminating power was made, it was generally regarded as important that the cooling of the gas, at any rate from 60° to about 25°, should take place slowly, if loss of illuminating power was to be avoided. With gas of the quality now usually made, this is, however, of but little influence, rapid cooling in this case effecting but little reduction of the illuminating power, provided the temperature is not reduced below 15°–20°; if, however, the gas is at any time cooled in presence of tar much below 15°, decided reduction in illuminating power occurs, and too great

reduction of temperature in condensation is, therefore, always to be avoided.

During the whole of condensation, including that occurring in the retort house, from 9 to 15 gallons of tar per ton of coal (varying with the nature of the latter and the temperature of carbonisation) are separated from the gas, together with a quantity of ammoniacal liquor varying usually from about 15 to 10 gallons per ton. These both flow together to the well or wells, to which any tar and liquor from the subsequent apparatus also gravitate. The condensed water removes a large proportion of the ammonia from the crude gas (usually about half of the 400–450 grains per 100 cub. ft. contained in the gas issuing from the retorts),

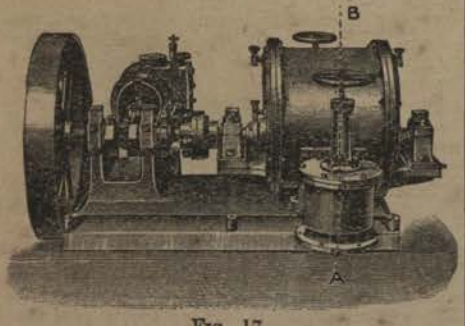


FIG. 17.

and the alkaline ammonia solution also extracts the whole of the hydrochloric acid in the gas formed from the chlorine in the coal, and some of the carbon dioxide, sulphuretted hydrogen, and hydrocyanic acid. The liquor obtained in condensation is termed 'virgin liquor,' that portion formed in the retort house being usually, though not invariably, weak, and containing from 0·5 to 1·5 p.c. of ammonia, whilst that from the condensers is more concentrated, and may contain 4 p.c. or more. The cooled gas mostly contains some 200 grains of ammonia, and 50–100 grains of hydrocyanic acid per 100 cub. ft., from 1 to 2 p.c. of sulphuretted hydrogen, and 1–3 p.c. of carbon dioxide, and in addition also an appreciable amount of tar fog, which has not been removed from the gas

FIG. 18.

in its passage through the condensers, and which, if not previously eliminated, is deposited in the subsequent purifying apparatus, rendering them much less efficient.

Exhausters. The gas pumps, or exhausters, are in the most usual practice placed at the outlet of the condensers, the gas being drawn through the condensers and forced on through the subsequent plant. Various kinds of exhausters are employed, the most popular being those of the Beale rotary type, shown in Figs. 17 and 18. These are automatically controlled by the vacuum in the hydraulic main so as to maintain the latter constant, a service pipe being run from the hydraulic main to a governor in the exhauster house. The latter governor is then connected with a throttle valve controlling the steam supply to the exhauster, so that the speed at which the latter runs is automatically regulated

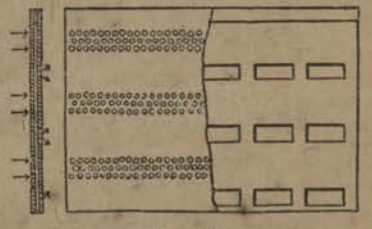


FIG. 19.

to give a steady vacuum, or the latter may be run at a constant speed, and the governor connected to a valve on a by-pass main from the inlet to the outlet of the exhauster, allowing more or less gas to flow back from the exhauster outlet to the inlet, according as the rate at which the gas is evolved from the retort falls or rises.

Extraction of tar fog. To eliminate the remaining tar fog from the cooled gas, two methods are employed. In the first, represented by the Pelouze-Audouin tar extractor, the gas is divided up into fine streams, which impinge, at a considerable velocity, on a flat surface; the tarry particles adhere to the latter and coalesce to tar which flows away. Fig. 19 shows the essential portion of the apparatus, which consists in two plates with a small space between them, the first of which is perforated with fine holes about $\frac{1}{35}$ inch in diameter, and the second with slots, the plates being so fixed that the gas issuing through the small holes impinges on the unperforated portion of the slotted plate. Two such pairs of plates are used in series, and these are arranged to form a bell (Fig. 20), which is sealed in the tar formed, and counterbalanced by weights so that it is free to rise in the tar. If the amount of gas passing through the apparatus increases, the pressure within the

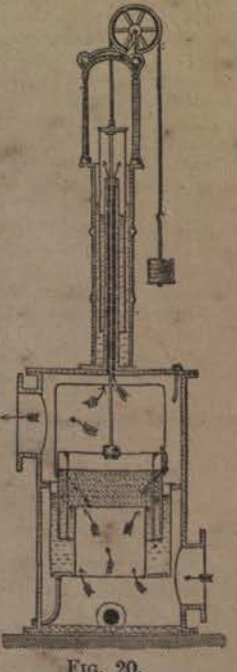


FIG. 20.

bell tends to increase also, and the latter rises, and thus presents a larger number of holes for the gas to pass through, and *vice versâ*, and in this manner the velocity of the gas through the holes is kept approximately constant with varying production of gas. This apparatus is very efficient when properly worked, but is preferably maintained at a temperature of about 30°, as otherwise the deposited tar may become so thick that it cannot flow away, and the apparatus becomes blocked.

The second method consists in dividing the gas into a number of small streams, and bubbling these through ammoniacal liquor, this serving the double purpose of removing tar fog, and of strengthening the weak liquor produced in other parts of the process (such as the retort-house liquor, or the liquor from the final scrubbers), which is fed into the apparatus. A very efficient apparatus of this type is the Livesey washer, the essential feature of which is shown in Fig. 21. It consists of a parallel series of troughs arranged in a cast-iron rectangular vessel, the lower portions of which are

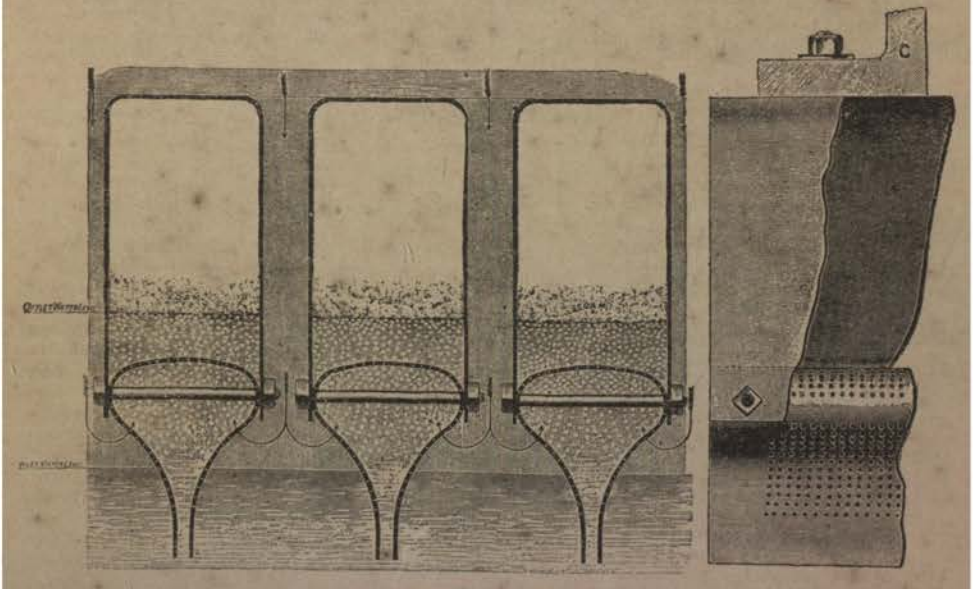


FIG. 21.

perforated with holes $\frac{1}{25}$ inch in diameter, as shown, this portion being sealed in ammoniacal liquor. The gas entering at the top passes down between the troughs, and forces some of the liquor through the holes into the interior of the troughs, thus unsealing the holes, through which the gas then bubbles, as well as through the second perforated plate across the width of the trough. The liquor in the trough is broken up into foam, and effects the removal of the tar fog and some ammonia from the gas, the washed gas passing away through the open end of the trough to the gas outlet. With proper working the amount of tar fog can be reduced to below 10 grains per 100 cub. ft., but the amount of ammonia removed varies greatly according to the strength of the liquor used, and the amount passed through the washer. Small amounts of carbon dioxide, sulphuretted hydrogen, and hydrocyanic acid are also removed by the washer.

Wet purification. To effect the complete, or almost complete, removal of ammonia, the gas is next washed with water in suitable apparatus, the washing being conducted on the counter-current principle, the gas meeting a current of water flowing in the opposite direction, so that the liquor leaving the apparatus meets with the gas richest in ammonia, and is thereby worked up to the highest strength possible, whilst the gas leaving the apparatus comes in contact with fresh water, containing little or no dissolved ammonia, and is thereby freed as completely as practicable from it. One of the oldest forms of apparatus for the purpose, which is still largely in use, is the *tower scrubber* (Fig. 22). This consists of a vertical tower of circular section filled with coke, flints, wooden boards on edge, or other material which exposes a large surface to the gas passing through it. Water is mechanically sprayed over the whole of the upper surface of the filling material, and slowly percolates downwards, meeting the ascending gas, and absorbing the ammonia it contains. The gas passes away from the top of the tower, and the liquor flows from the bottom through a siphon or seal-pot to a special tank or direct to the storage well. Such scrubbers are frequently worked in pairs, the first being fed with weak liquor from other parts of the process, but the final washing must always be effected with fresh water if anything like complete elimination of the ammonia is to be effected. Provided the tar fog has been previously removed from the gas, these scrubbers form very effective pieces of apparatus, especially where boards on edge are employed for filling, but if tar is allowed to get forward into them, their efficiency is greatly reduced, as the down-flowing water then ceases to flow uniformly over the whole surface, but

goes in channels, and the gas is not brought in proper contact with the water.

In place of these scrubbers, mechanically actuated rotary washers are now largely used. Several efficient types are in use, one of which, viz. Kirkham, Hulett, and Chandler's 'standard'

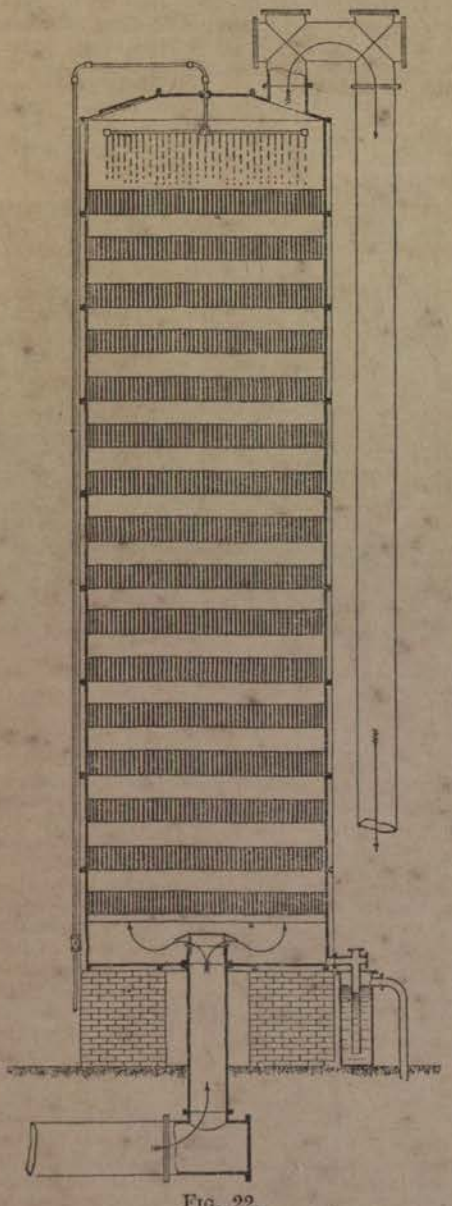


FIG. 22.

washer, is illustrated in Fig. 23. This consists of a horizontal cylindrical vessel, divided internally into compartments by vertical plates, the latter having openings, where necessary, to allow of the passage of the gas. In each compartment is a disc keyed to the central revolving shaft, the disc, with the exception of the central portion, being filled with bundles of thin wooden boards or sheet-iron plates, fixed together in such a manner as to allow free passage of the gas over their surface. The gas, in traversing the apparatus as shown by the arrows, passes over this surface, which is kept wetted by revolving through the liquor in the bottom of each compartment, and effects the removal of the ammonia. The washing water enters at the gas outlet end, and flows continuously through each compartment, becoming continuously stronger to the opposite end of the washer, and away from that end by means of a siphon to the storage well. The Holmes washer, which is largely in use, resembles the foregoing in main outline, but special brushes are used to form the necessary washing surface.

Provided that the gas is properly cooled, and that the temperature of the incoming water is also low, the quantity of ammonia left in the gas should not exceed 1–2 grains per 100 cub. ft. In hot weather, however, or with insufficient cooling of the gas, this amount may be considerably exceeded, owing to the lessened solubility of ammonia in water at higher temperatures.

Naphthalene removal. Mention has already been made of the difficulty which arises from blockages both in the plant and mains on the works and on the mains and services in the district of supply, from the deposition of solid naphthalene from the gas. In the early days of the industry, when lower carbonisation temperatures were employed, no difficulty was experienced in this respect, as, although considerable amounts of naphthalene were even then present in the hot gas, the amount of other tar constituents boiling at the same or a lower temperature than naphthalene was sufficient to effect a practically complete washing out of the naphthalene from the gas in the ordinary process of condensation. As carbonising temperature increased, trouble from naphthalene became more and more noticeable, at first only where coals from the Durham coal-field were carbonised, but eventually, with still higher carbonising temperatures, from all classes of coal, and very serious nuisance from naphthalene stoppages took place, both manufacturers and consumers being affected.

The difficulty arises from the fact already discussed, that increased carbonising temperatures, when there is also a considerable free space above the coal in the retort, effect an increase in the production of naphthalene and a decrease in the production of lower-boiling tar oils, the proportion of the latter being then insufficient to effect the complete washing out of the naphthalene from the gas at the cold end of the condenser, and the gas may, therefore, leave the latter almost saturated with naphthalene vapour at the temperature of the condenser outlet, such gas then becoming supersaturated on further cooling in the works or district of supply, and then under favourable conditions depositing solid naphthalene, mostly in the form of very bulky flaky crystals, a very small weight of which is capable of causing a serious block.

In some cases it has been possible, by modification of the condensing system, to effect a sufficient removal of naphthalene in the latter to avoid further trouble, but the increase in

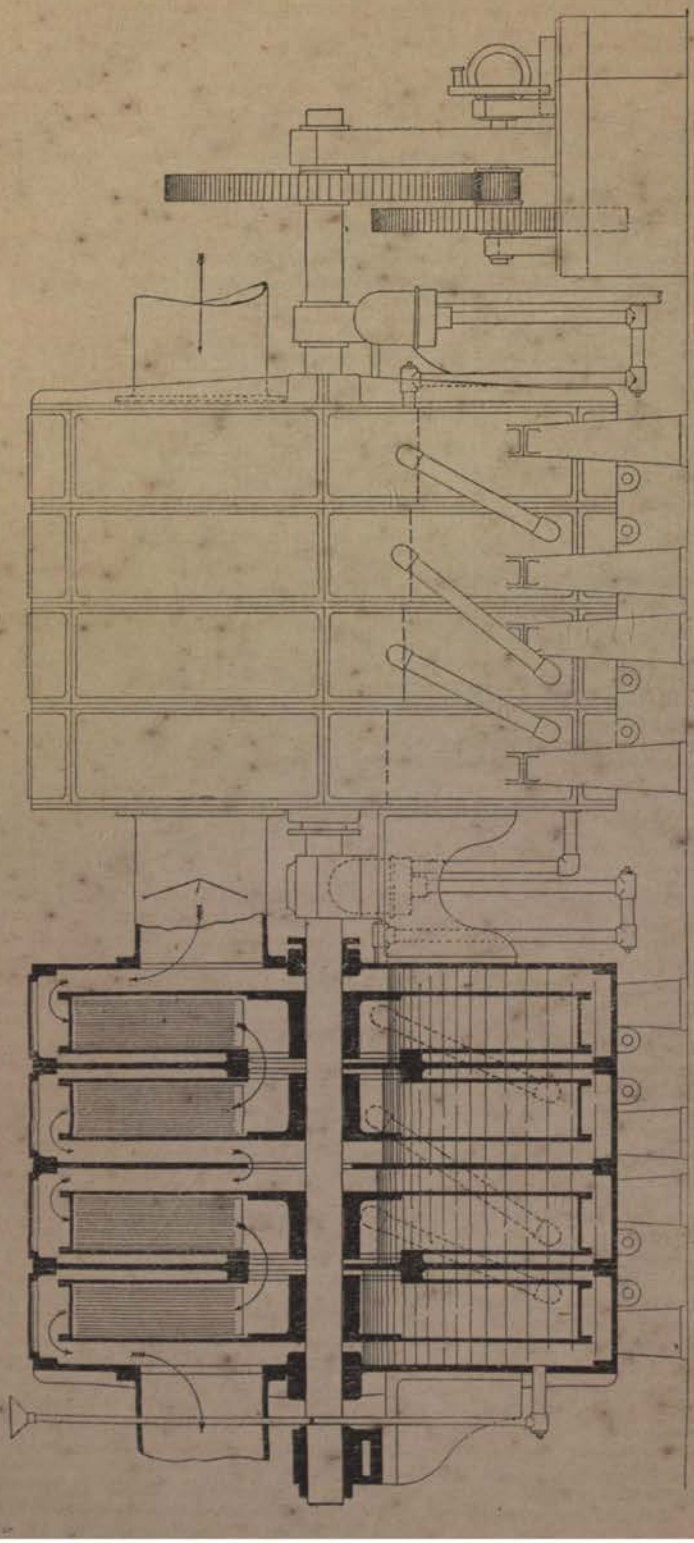


Fig. 23.

carbonising temperatures during recent years has brought about such a reduction in the amount of light oils produced, that this is now rarely possible, and some further treatment of the gas is therefore requisite in many cases. With vertical retorts, however, and also where horizontal retorts are charged nearly full, a greatly increased production of light oil occurs, and in these cases the ordinary condensation process is, in many instances, sufficient to prevent naphthalene trouble, without any subsequent process.

Two methods of treatment are employed, the one consisting in washing the gas with suitable naphthalene solvents, whereby its amount in the gas is largely reduced, and the second by adding to the gas the vapours of liquids which dissolve naphthalene, and have a somewhat similar vapour pressure. If, after such treatment, any naphthalene subsequently condenses from the gas, a simultaneous condensation of the added vapours occurs, and these dissolve the naphthalene so that the latter condenses in the liquid state, which causes no trouble, as provision is always made for the collection of liquids which may separate, these gravitating down to siphons fixed at intervals at low points in the mains, which are pumped at regular intervals.

To wash the naphthalene from the gas, any of the forms of washer employed for ammonia may be used. As solvent oil, the heavy oil fraction of coal tar, boiling at

270°–350° (green oil), was first suggested by Young and Glover (Eng. Pat. 20125, 1896); but as this oil also dissolves benzene, and would reduce the illuminating power of the gas, from 3 to 6 p.c. of benzene is added to the green oil, which prevents any such action. The same oil was also proposed at a later date in Germany by Bueb, and is largely employed there.

To increase the vapours of liquid hydrocarbons in the coal gas, Bunte and Eitner (J. Gasbeleucht. 1892, 569; 1899, 73) added xylene vapour to the gas, and Colson (Eng. Pat. 17666, 1904) and Bell (J. Gas Lighting, 1904, 88, 98) add the fraction of coal tar boiling chiefly between 170° and 210°. Many other washing oils are used, which frequently act in both the ways above described, partly dissolving naphthalene from the gas, and partly volatilising low-boiling constituents into the gas. Thus, for example, the tar obtained in the manufacture of carburetted water gas is now largely used for the purpose, as this contains a good percentage of light oils, which are largely volatilised into the gas, whilst the residual oil extracts much naphthalene from the gas. In other cases ordinary paraffin oil is used, some of which also volatilises into the gas.

Botley (Eng. Pat. 9316, 1896) sprays a fine mist of paraffin oil into the gas leaving the works, this spray being carried right to the extreme of the district and also tending to prevent the deposition of naphthalene in the solid state, a similar effect being produced by volatilising paraffin vapour into the gas, which, by its quick condensation, also produces a mist.

The naphthalene washing process is mostly carried out on the cooled gas, either before or after the washing and scrubbing plant; in some cases, however, the washing process with water-gas tar takes place on the hot gas before the condensers, in which case a larger amount of oils are volatilised into the gas from that tar, and partly condense again in the condensers, and assist in washing out the naphthalene remaining in the gas.

Dry purification. The gas leaving the scrubbers still contains from 0·8 to 2·0 p.c. of sulphuretted hydrogen, and from 1 to 3·5 p.c. of carbon dioxide, together with smaller amounts of other impurities, namely, from 10 to 80 grains of sulphur per 100 cub. ft. as organic sulphur compounds, chiefly carbon disulphide, and from 50 to 100 grains of hydrocyanic acid. Of these the sulphuretted hydrogen, which on combustion is converted into sulphur dioxide, must be removed to an extent which is practically complete, statutory provision being made to this effect in all Acts of Parliament controlling gas undertakings. The carbon dioxide is not in itself deleterious, but was formerly frequently

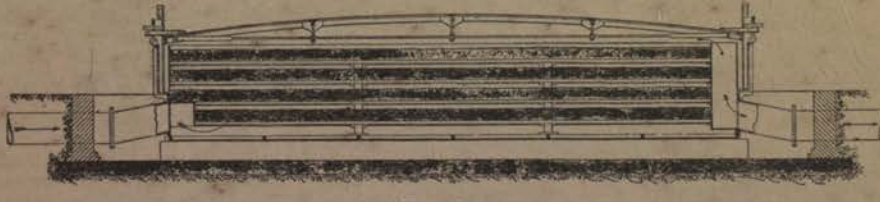


FIG. 24.

removed, as its presence materially reduces the illuminating power of the gas, each 1 p.c. of carbon dioxide lowering the illuminating power from 3 to 4 p.c. It also lowers the calorific power, but in much smaller proportion (1 p.c. for each 1 p.c. of CO_2 present), and in view of the decreasing importance of illuminating power, the removal of the dioxide is now practised to a much smaller extent than formerly. The removal of the sulphur compounds other than sulphuretted hydrogen cannot be effected completely by any known process, but many undertakings were formerly compelled by statute to reduce the amount of these to a certain maximum limit, varying from 17 to 30 grains per 100 cub. ft., but these clauses have been now repealed, and, unless the amount of these is high, no attempt is now made to remove them in most works. The hydrocyanic acid is extracted more or less completely along with the sulphuretted hydrogen by all the processes in use, and is not often found in the purified gas to any considerable extent. In some few undertakings the hydrocyanic acid is extracted at an earlier stage by special processes in order to obtain cyanogen compounds in marketable form, and the methods employed for this purpose will be described later.

Where sulphuretted hydrogen alone is to be removed, the purifying material employed is moist hydrated ferric oxide, the naturally occurring bog iron ore being largely used for the purpose. This contains a sufficient amount of fibrous organic matter to render the mass porous and allow of the passage of the gas through it. Where artificial or natural ferric hydroxides, free from organic matter, are employed, these are mixed with material such as sawdust or wood chips to give the required porosity.

The material is charged in even layers into rectangular cast-iron vessels (Fig. 24) containing wooden grids to carry the oxide, the thickness and number of the layers varying according to the size of the purifier. The latter is then closed by a lid, which, in the diagram shown, is rendered gas-tight by the provision of vertical sides which drop into a water lute cast around the periphery of the purifier; so long as the pressure of the gas within the box does not exceed that equal to the depth of the water seal, no gas can escape. As, however, serious explosions have occurred through escape of gas through the water seal, owing to excessive pressure, the present tendency is to the adoption of luteless lids which are bolted to the purifier and made gas-tight by the insertion of a rubber joint between the purifier and cover.

The purifiers are mostly worked in sets of four, the connections being so arranged that the

gas can be allowed to enter any box, and then pass in series through the remaining boxes. Frequently only three boxes are worked in series, the fourth being off for changing the material, or kept in reserve when freshly charged until sulphuretted hydrogen is found to be getting forward nearly to the outlet of the box before it, when the fresh box is put to work, and the first box in the series shut out and recharged with fresh oxide.

The sulphuretted hydrogen acts on the hydrated ferric oxide in two different ways, forming either ferric sulphide or a mixture of ferrous sulphide and free sulphur:

(1) $Fe_2O_3,xH_2O+3H_2S=Fe_2S_3+(x+3)H_2O$.
(2) $Fe_2O_3,xH_2O+3H_2S=2FeS+S+(x+3)H_2O$.

In neutral or faintly acid condition, the reaction takes place according to the second equation, but in slightly alkaline condition ferric sulphide alone is formed, and as the coal gas entering the purifiers always contains traces of ammonia, it is this compound which is chiefly formed in the gas purifiers.

When the mass has ceased to absorb sulphuretted hydrogen, it is removed from the purifier and spread out on the floor in moist condition, with occasional turning over, to expose it to the air, when the ferric sulphide is oxidised, reforming hydrated ferric oxide, with separation of free sulphur. As soon as this reaction is complete, the mass can be returned to the purifier for the extraction of further amounts of sulphuretted hydrogen, this alternate process of fouling and revivification being continued until the mass contains 50–70 p.c. of sulphur, when it is sold for its sulphur content, being chiefly used for sulphuric acid manufacture, one advantage of the material for this purpose being its almost complete freedom from arsenic.

As the crude gas entering the purifiers always contains some oxygen, the revivification of the ferric sulphide to ferric oxide and sulphur always takes place to some extent in the purifier itself, and the length of time for which a purifier will run without changing depends, to a large extent, on the amount of oxygen in the crude gas. All things considered, the volume of oxygen most suitable is rather more than half the percentage volume of the sulphuretted hydrogen in the crude gas; and where the air accidentally getting in to the gas does not reach this amount, more is added. A still larger addition of air further increases the time the purifiers will run without changing, and consequently the cost for labour, but the extra amount of oxygen and nitrogen remaining in the gas lowers its quality, and if too much oxygen is present the separated sulphur may even fire in the boxes, and, apart from the damage caused in the box, the gas may be badly contaminated with sulphur dioxide. The temperature of the gas passing through the purifiers should not fall below about 15°, as then the action of the oxygen becomes very slow.

Instead of working the rotation of the purifiers in the manner mentioned above, which was formerly universal, modified methods are now frequently adopted. Thus, for example, instead of putting on a fresh box as the last in the series, it is now frequently put on as the first box, where it removes practically the whole of the sulphuretted hydrogen, and the gas coming from the outlet of the two boxes last in the series becomes quite free from sulphuretted hydrogen in a short time, any sulphuretted hydrogen passing from the last purifier during this period being taken up by a 'catch' purifier placed on the common outlet main. At intervals of 24 or 48 hours or more, the last box is made the first box of the series, when the same change occurs, and this process of 'reversed' rotation continued. Working in this manner, it is often possible to keep the gas free from sulphuretted hydrogen for a very long period, and to obtain a high percentage of sulphur in the spent oxide without removing the material from the box, and, indeed, it often happens that a removal of the material is necessary, not on account of its passing sulphuretted hydrogen, but because the mass has become so dense from separated sulphur, that it requires an undue pressure to force the gas through it. The exact reasons for the longer period of working are not yet quite clear, though it is evident that this method of working enables the oxygen in the crude gas to effect a quicker revivification of the ferric sulphide than is the case with the older method of working.

Purification from carbon dioxide after removal of sulphuretted hydrogen. When the carbon dioxide is required to be removed from the gas after freeing from sulphuretted hydrogen, a similar set of two, three, or four purifiers is employed, into which slaked lime is charged in place of the hydrated ferric oxide. This is prepared by slaking good non-hydraulic lime with water, which is added in sufficient quantity to moisten the slaked lime produced to such an extent that it just balls together when squeezed in the hand. This removed the whole of the carbon dioxide from the gas, the slaked lime being converted into calcium carbonate

$$Ca(OH)_2+CO_2=CaCO_3+H_2O.$$

Where the gas is free from sulphuretted hydrogen, the spent lime obtained is fairly innocuous, though of very little value, but is sometimes reburnt to lime and again used for purification.

Simultaneous removal of sulphuretted hydrogen, carbon dioxide, and carbon disulphide by means of lime. The dry purification process described above hardly effects the removal of sulphur compounds other than sulphuretted hydrogen to any material extent, and the great bulk of these remains in the purified gas, and much controversy has occurred as to whether these should be removed as far as possible or not. Whilst it is not disputed as an abstract proposition that it is desirable to reduce the amount of sulphur in the gas to as low a limit as is practicable, the difficulty in the matter lies in the fact that the only process, as yet known, by which this can be even partially effected at a reasonable cost on the large scale has many serious drawbacks. This process consists in subjecting the gas to the action of calcium hydrosulphide formed by the action of sulphuretted hydrogen on lime, which absorbs a large proportion of the carbon disulphide, and by which means the total amount of sulphur left in the gas can be reduced to 12–20 grains per 100 cub. ft. The objections to this process are as follows: (1) the spent material consists of a sloppy mass containing calcium sulphide, having

a very unpleasant smell of sulphuretted hydrogen, &c., which is perceptible at long distances from the works, and occasions complaints in their neighbourhood, and also in districts through which the material may have to be carted. (2) The discharging of the spent material from the boxes is exceedingly unpleasant to the men employed in the operation, and not unattended with danger to their health. (3) The process is somewhat uncertain in action, and under some conditions the material may not only not absorb any carbon disulphide from the gas, but may also give off that previously absorbed, thus rendering the amount of sulphur in the gas far higher than it would have been with oxide purification only. (4) Great difficulty is experienced in disposal of the spent material, except in smaller undertakings, in agricultural districts, where there is a limited demand for the material for manurial purposes.

Formerly a number of works were statutorily compelled to reduce the total amount of sulphur in their gas below a certain maximum, but these restrictions have now been abolished in most cases as a result of a Board of Trade inquiry, under the presidency of Lord Rayleigh, held in 1904, the only restriction now being with regard to sulphuretted hydrogen, which must still be completely removed. There is now a fairly general, though not universal, opinion, that so long as the amount of sulphur in the gas does not exceed 35–40 grains per 100 cub. ft., the disadvantages accruing from the adoption of the lime process more than counterbalance the advantage of reducing the sulphur compounds to a lower limit in the majority of works, and the process is now, in most cases, only adopted in works where the sulphur compounds, other than sulphuretted hydrogen, are exceptionally high.

In carrying out the lime process, the method most commonly adopted is to pass the gas containing the carbon dioxide, sulphuretted hydrogen, and carbon disulphide through a set of at least four purifiers, worked in rotation in a similar manner to the first method described in connection with oxide of iron purifiers. In such a set of four purifiers the first box in the series, which has previously been successively fourth, third, and second box, is nearly spent, but absorbs a certain amount of carbon dioxide, as the latter, being a stronger acid than either sulphuretted hydrogen or carbon disulphide, combines with the compounds these have formed with lime, viz. calcium hydrosulphide and thiocarbonate, and liberates the former gases, forming calcium carbonate, so that carbon disulphide is often found in larger quantity at the outlet of the first box than at the inlet. In the second box, some free lime is usually present, and a fair amount of carbon dioxide and small amounts of sulphuretted hydrogen are absorbed; but the greatest absorption occurs in the box third in series. Here the whole of the carbon dioxide and a large proportion of the sulphuretted hydrogen are absorbed, and the calcium hydrosulphide formed from the latter absorbs, in proper working, much of the carbon disulphide. The fourth box absorbs the remainder of the sulphuretted hydrogen, and more of the carbon disulphide. The gas from the latter purifier passes to a catch box of oxide of iron, and when the fourth box passes much sulphuretted hydrogen, the box first in series is discharged, recharged with fresh lime, and put on as the last in series.

For the effective removal of the carbon disulphide, one of the most important factors is the amount of oxygen present in the crude gas. If this is excessive, the calcium hydrosulphide is oxidised to thiosulphate, &c., as fast as it is formed, and before it can act on the disulphide, and no removal of the latter occurs; moreover, if the purifiers have been previously extracting the disulphide and the amount of oxygen in the crude gas suddenly rises, not only is no carbon disulphide absorbed, but that previously retained in the lime is given off by the action of the carbon dioxide, and the 'purified' gas may contain three or four times as much disulphide as is present in the gas entering the purifiers. On the other hand, if oxygen is entirely absent, no absorption of carbon disulphide takes place, the most regular results being obtained when the average amount of oxygen present is equal to about one-third of the average volume of sulphuretted hydrogen in the crude gas. Even when this condition is maintained, a good absorption does not invariably occur, and from causes which are at present unknown, a set of purifiers may sometimes cease to absorb the disulphide, and will then usually not recover their activity until they are all recharged with fresh lime.

The exact nature of the compound which combines with the disulphide is not yet known with certainty. It was formerly thought that calcium hydrosulphide combined with it, forming calcium thiocarbonate

$$Ca(SH)_2+CS_2=CaCS_3+H_2S;$$

but calcium hydrosulphide, and, indeed, all the soluble hydrosulphides, when free from polysulphides, combine very slowly, if at all, with carbon disulphide in absence of oxygen. Veley (Chem. Soc. Trans. 1885, 47, 478) suggests that the active compound is calcium hydroxyhydrosulphide Ca(OH)(SH), but the writer regards it as much more probable that the real absorbent is calcium disulphide CaS_2, formed from the hydrosulphide by oxidation:

$$Ca(SH)_2+O=CaS_2+H_2O;$$

for although the pure sulphides and hydrosulphides of potassium, sodium, ammonium, and calcium scarcely unite with carbon disulphide at the ordinary temperature, the disulphides of the above metals in all cases combine rapidly and completely with it, forming *perthiocarbonates*, such as Na_2CS_4 (Gélis, Compt. rend. 81, 282). This supposition explains why some oxygen is necessary for carbon disulphide absorption, as it is required to effect the formation of polysulphide from the primary hydrosulphide, whilst excess of oxygen oxidises the latter to thiosulphate, &c.

Under the most favourable conditions, the whole of the carbon disulphide cannot be removed from the gas, and there are always, in addition, some 6–10 grains of sulphur present in the form of other organic sulphur compounds, amongst which mercaptans, alkyl sulphides, and thiophen have been detected, as well as carbonyl sulphide COS, the last, however, being removed

with the carbon disulphide. It is rarely possible to reduce the total sulphur below about 10 grains per 100 cub. ft.

It will be seen that this process involves the complete removal of carbon dioxide from the gas, whether this is otherwise desirable or not, and an economical reliable process free from the objections inseparable from lime purification, and which does not necessitate the removal of carbon dioxide, is much to be desired, but has not hitherto been discovered, although many suggestions have been made. By reheating the gas to about 300°–350°, the carbon disulphide is largely converted into sulphuretted hydrogen, which may be removed by again purifying the gas, after cooling, with ferric oxide. This method of removal was proposed more than 50 years ago by Bowditch, but the practical difficulties in large scale working prevented its adoption, although it is stated that the process has been carried out successfully in the United States. A further suggestion has been to wash the gas with aniline or to pass the gas through ferric oxide moistened with aniline, which combines with the carbon disulphide, forming thicarbanilide, but the cost of this process is prohibitive.

A solution of ammonium polysulphide was found by Claus and Watts (J. Soc. Chem. Ind. 1887, 6, 27; Eng. Pats. 7585, 1886; 3267, 1887) to effect the removal of carbon disulphide, and this has been confirmed by others, but it has hitherto been found that the absorption is not regular, varying from time to time for reasons which have not yet been elucidated. As with the lime process, the first action is probably the formation of ammonium perthiocarbonate $(NH_4)_2CS_4$, but this is an exceedingly unstable substance, and very readily decomposes with evolution of CS_2. It is, however, capable of undergoing another change, yielding ammonium thiocyanate

$$(NH_4)_2CS_4 = NH_4CNS + 2H_2S + S,$$

and if the conditions under which this change takes place quickly and with certainty could be ascertained, and then economically maintained, this should form a good and cheap process for the purpose.

The Cooper liming process (Eng. Pat. 5713, 1882), in which small quantities of lime are added to the coal before carbonisation, although primarily intended to increase the yield of ammonia, also effects a reduction in the amount of carbon disulphide; but the large scale experiments with the process made about thirty years ago were abandoned, chiefly on account of the deterioration in the quality of the coke produced. Paterson & Twycross (Eng. Pat. 26772, 1910) have introduced a modified method, whereby a regulated amount of powdered lime is distributed evenly over the surface of the coal on its way to the retort, the powder being made to adhere by the action of a small jet of steam. The process has been at work for some months at the Cheltenham Gas Works, using about 2 per cent. of lime, and has not resulted in any material deterioration of the coke, and has given an increased yield of ammonia, whilst the amount of sulphur other than sulphuretted hydrogen in the gas has averaged 20 grains per 100 cub. feet, as compared with more than double this amount when the liming is omitted.

Removal and recovery of cyanogen compounds. It has long been known that crude coal gas contains cyanogen derivatives, and that their quantity tends to increase with increasing carbonising temperatures. The only compound of this kind that has been detected with certainty in the gas is hydrocyanic acid, although it is possible that cyanogen itself may be present in small quantity. The total amount varies considerably at different works, but with the temperatures at present mostly employed, the amount of hydrocyanic acid produced in the gas issuing from the retorts averages about 120–130 grains per 100 cub. ft., of which about one quarter is removed in the virgin liquor during condensation, partly as ammonium cyanide, but chiefly as ammonium thiocyanate, into which the cyanide formed also passes on storage. Smaller amounts are absorbed in a similar manner in the washers and scrubbers, but with high retort temperatures from 90–100 grains of hydrocyanic acid per 100 cub. ft. (equivalent to about 4–4·5 lbs. of crystallised sodium ferrocyanide $Na_4FeCy_6,10H_2O$ per ton of coal) usually remain in the gas entering the purifier.

Where lime alone is used for purification, the hydrocyanic acid is completely absorbed with the other impurities, and converted into calcium thiocyanate; and where ferric oxide is used, the greater quantity is likewise absorbed with formation of insoluble iron ferrocyanides and double ferrocyanides of iron and ammonium (crude Prussian blue) as well as ammonium thiocyanate. The more complete the removal of ammonia from the gas before the purifiers, the greater is the amount converted into ferrocyanide, and the smaller the production of thiocyanate.

The greatly increased demand for cyanide following on the introduction of the McArthur-Forrest cyanide process for extraction of gold from the mine 'tailings,' resulted in many attempts being made for the utilisation of the cyanogen compounds in the crude gas. At first the spent oxide was utilised for this purpose, being sold to chemical manufacturers for its Prussian-blue content, where this reached an amount of 6–8 p.c. A number of processes were also devised for the special recovery of the hydrocyanic acid by extracting it from the gas before the latter reached the purifier. In these processes the hydrocyanic acid is recovered either as (1) ferrocyanide or (2) thiocyanate. For the former, the gas is washed with a solution containing alkali and ferrous hydroxide, carbonate, or sulphide in suspension, which absorbs the hydrocyanic acid with production of the ferrocyanide of the alkali used, the reaction with ferrous sulphide and sodium carbonate, for example, being:

$$FeS + 2Na_2CO_3 + 6HCy = Na_4FeCy_6 + H_2S + 2H_2O + 2CO_2.$$

Where ammonia is used as the alkali, as in the processes of Rowland (Eng. Pat. 22347, 1891), Bueb (Eng. Pat. 9075, 1898), and Lessing (Eng. Pat. 2090, 1907), the gas is treated before the removal of ammonia in a suitable washer with a strong solution of ferrous sulphate, which is converted first into ferrous sulphide and ammonium sulphate by the sulphuretted hydrogen and ammonia of the crude gas, and then yields ammonium ferrocyanide. The latter

solution is unstable, and to a large extent combines with the excess of iron present, yielding insoluble double ferrocyanides of iron and ammonium, the proportion of insoluble ferrocyanides produced increasing with increasing strength of the ferrous sulphate solution used. The sludge obtained, containing chiefly crude Prussian blue, with the excess of unused ferrous sulphide, is sold to chemical manufacturers for conversion into saleable ferrocyanide or cyanide.

Where a fixed alkali is used (soda and lime being the only ones available, on account of price), the gas is treated after the removal of ammonia in a washer fed with a mixture of sodium carbonate and ferrous carbonate (Knublauch, Eng. Pat. 15164, 1887), or a solution of ferrous sulphate with excess of lime, when the bulk of the hydrocyanic acid is absorbed and converted chiefly into the soluble sodium or calcium ferrocyanide, only small amounts being converted into insoluble ferrocyanides. The sodium ferrocyanide solution, after filtration from the excess of ferrous sulphide, &c., is directly evaporated and crystallised; the calcium ferrocyanide solution, on the other hand, is unstable when heated, and is preferably first converted into the sodium salt, by addition of the requisite quantity of sodium carbonate, or, if the potassium salt is required, the calcium ferrocyanide solution may be treated with potassium chloride solution, when the sparingly soluble calcium potassium ferrocyanide CaK_2FeCy_6 is precipitated, and after filtration may be converted into a pure solution of potassium ferrocyanide by addition of the requisite amount of potassium carbonate. In the Davis-Neill process (Eng. Pat. 26566, 1901), the treatment with sodium and ferrous carbonate is carried out before the removal of ammonia from the gas, and the liquor from the washer first distilled to recover ammonia.

In all these processes, a certain amount of hydrocyanic acid is converted into thiocyanate, the proportion formed being greater when ammonia is present, and *carbonyl ferrocyanides* are also usually produced to some extent. Carbonylferrocyanic acid $H_3Fe(CO)Cy_5$ may be regarded as ferrocyanic acid in which 1 molecule of HCy is replaced by the radical CO, the formation of these salts being doubtless due to the presence of carbon monoxide in the gas treated. They have little or no commercial value, and accumulate in the mother liquors, being very soluble in water.

For the recovery of the hydrocyanic acid as thiocyanate, according to the British Cyanide Co.'s process (Eng. Pat. 13653, 1901), the gas, whilst still containing ammonia, is passed through a washer containing water or ammoniacal liquor, to which free sulphur is periodically added. The ammonia and sulphuretted hydrogen dissolve in the water, forming ammonium sulphides, which dissolve the sulphur, yielding ammonium polysulphide solution, and the latter absorbs the hydrocyanic acid, forming ammonium thiocyanate. So long as free sulphur is present, the formation of polysulphide and of thiocyanate continues, and a solution can be obtained containing from 3 to 5 lbs. of ammonium thiocyanate per gallon. Except for volatile ammonium salts, such as sulphide, which are expelled on heating, the solution is comparatively pure, and is sold for conversion into cyanide.

Other purification processes. As already mentioned, a portion of the sulphuretted hydrogen and carbon dioxide is removed along with the ammonia, the solution of the latter in water absorbing these acid gases with formation of ammonium sulphides and carbonates, but the amount of ammonia present is much below that required for their complete removal. Many attempts have been made to modify the scrubbing process in such a manner as to effect the complete removal of these two impurities. Hills (Eng. Pat. 1369, 1868; 934, 1874; 1895, 1875) showed that when the ammoniacal liquor is heated to about 90°, it gives off large quantities of carbon dioxide and sulphuretted hydrogen, but only small amounts of ammonia, the residual liquor then containing large amounts of free ammonia, which may be used for washing a further amount of the acid gases from crude gas. A modification of Hills' method has been described by Holgate (J. Gas Lighting, 1895, 65, 1133). Claus (Eng. Pat. 2838 and 2865, 1881; 4644, 1882; 5959, 1883) combined Hills' process with the continuous distillation of a large amount of liquor, the ammonia being returned to the gas, so that the amount of ammonia in the gas in the scrubbers was four or five times that normally present, and was enabled, on a moderate scale, to effect in this manner a complete removal of the sulphuretted hydrogen and carbon dioxide from the gas, doing away with the necessity for any further dry purification. By washing also with a solution of ammonium polysulphide, the amount of hydrocyanic acid and carbon disulphide were largely reduced. The mixed sulphuretted hydrogen and carbon dioxide evolved from the heated liquor were, after recovery of the ammonia present by washing with water or acid, mixed with just sufficient air to convert the sulphuretted hydrogen into sulphur and water, and passed through heated ferric oxide in the 'Claus kiln,' the sulphur produced being condensed in suitable chambers.

Great hopes were entertained as to the success of the process, but, unfortunately, the practical difficulties of working which manifested themselves when the process was tried on a larger scale have never been overcome, and at Belfast, where the process was tried for many years, it was not found possible to regularly effect complete removal of the sulphuretted hydrogen, and the loss of ammonia was very considerable (J. Gas Lighting, 1897, 69, 1475).

In coke-oven plants, the ammonia is now frequently directly recovered as sulphate, by washing the gas, freed from tar, with dilute sulphuric acid, and this procedure is also adopted in some small gas undertakings (Moon, J. Gas Lighting, 1910, 112, 474). At the present time also processes are on trial on the large scale for the recovery of the ammonia from the gas direct as sulphate by utilising the sulphuretted hydrogen of the crude gas as the source of the sulphuric acid. In Burkheiser's process (Eng. Pat. 20920 and 21763, 1908; 17359, 1910), the gas, after cooling and removal of tar fog, and when still containing the ammonia, is passed through small oxide-of-iron purifiers containing a porous ferric oxide with some combined water, which are kept at 60°, and removes the whole of the sulphuretted hydrogen.

Simultaneously, a current of air and steam is led into a purifier previously in use and saturated with sulphuretted hydrogen, when the sulphur burns, forming a mixture of sulphur dioxide and trioxide, and the gases from each purifier, the one consisting of gas with all the ammonia and the other of nitrogen mixed with sulphurous gases, are led to two separate scrubbers. A solution containing ammonium sulphate is allowed to flow down the scrubber treating the latter, and absorbs the sulphur dioxide and trioxide, forming a solution of ammonium hydrogen sulphate and ammonium hydrogen sulphite, which is pumped to the top of the first scrubber through which the coal gas containing ammonia is passing, and absorbs the ammonia, reforming the normal sulphate and sulphite. This circulation of the liquor to the air scrubber and gas scrubber is maintained, and the solution becomes saturated, and crystals separate out and are removed as they separate, the settled liquor continuing in circulation. In this manner the ammonia is recovered as a mixture of about two-thirds sulphate and one-third sulphite, which may be either used direct as manure or converted into pure sulphate.

In the Feld process (Eng. Pat. 3061, 1909), the cooled gas, freed from tar fog but containing all the ammonia and sulphuretted hydrogen, is passed through a solution of ferrous sulphate, yielding ammonium sulphate and ferrous sulphide

$$2NH_3+H_2S+FeSO_4=(NH_4)_2SO_4+FeS.$$

The mixture is then treated with sulphur dioxide, when the ferrous sulphide dissolves, yielding thiosulphate and polythionates of iron, this solution being again subjected to the action of the crude gas, when ferrous sulphide is reformed, together with the ammonium salts of the thio-acids. The alternate treatment with sulphur dioxide and crude gas is continued till the solution of ammonium salts becomes concentrated, when, after final treatment with sulphur dioxide, it is heated, the thionates being decomposed with formation of ammonium and ferrous sulphates, and separation of sulphur. The latter is filtered off and utilised for the preparation of the sulphur dioxide, and the filtrate treated with crude gas to convert the ferrous sulphate into ammonium sulphate and ferrous sulphide; the latter is separated and again used in the process, the solution of ammonium sulphate being evaporated and crystallised.

Yield of gas and by-products. The volume of gas obtained varies naturally to a considerable extent, according to the quality of the coal carbonised, to the conditions of carbonisation, and also to the extent to which the furnace gases, consisting chiefly of nitrogen, are drawn into the gas through the porous retorts. At the present day the volume of gas produced from a ton of coal, measured moist at 60°F. and 30 inches bar., usually falls within the limits of 9000 and 13,000 cub. ft., and, except in small works, or where gas of high illuminating power is produced, the yield does not often fall below about 11,000 cub. ft. From the same classes of coal, the higher the yield of gas the lower is the illuminating power and calorific power, but, in general, the total yield of light represented by the multiple of make per ton × illuminating power, becomes higher as the make of gas increases, and this is the case to a still greater extent with the yield of heat units per ton of coal, as the calorific power falls off with increasing gas production to a much smaller extent than is the case with the illuminating power; and, in view of the fact that the heating value of the gas is now by far the most important factor, there is a constant endeavour to obtain as high a yield as possible.

The constituents present in purified coal gas in more than minute quantity are carbon dioxide, ethylene, benzene, oxygen, carbon monoxide, methane, hydrogen, and nitrogen. Their relative proportions naturally vary considerably, but for the most part fall within the following limits:—

Carbon dioxide	0·0–3·0 p.c.
Ethylene	2·0–4·0 ,,
Benzene	0·5–1·0 ,,
Oxygen	0·0–1·5 ,,
Carbon monoxide	4·0–11·0 ,,
Methane	25·0–35·0 ,,
Hydrogen	43·0–55·0 ,,
Nitrogen	2·0–12·0 ,,

The ethylene and benzene are usually estimated together and recorded as "unsaturated hydrocarbons," no very satisfactory quick method for their separate determination being available. In addition to methane, the richer coal gases contain small amounts of ethane, which is, however, also difficult of estimation in ordinary analyses. The nitrogen is usually taken as the difference between the sum of the other constituents and 100. The sp.gr. of coal gas falls mostly within the limits 0·4 and 0·5 (air=1), and at the present time is generally between 0·4 and 0·45.

The yield of coal tar varies commonly from 9 to 13 gallons per ton of coal, averaging about 10 gallons, or some 5·5 p.c. of the weight of the original coal. Its sp.gr. varies from about 1·15 to 1·25, this depending largely on the temperature of carbonisation. The higher the temperature to which the volatile products are exposed, the higher is the average carbon percentage, and the lower the hydrogen percentage of the tar, and the greater the amount of the so-called 'free carbon' formed; the latter, although in appearance resembling amorphous carbon, always contains hydrogen, and consists of derivatives of very complex hydrocarbons, which are infusible and insoluble in the remaining tar. The tar from vertical retorts is much thinner, and has a sp.gr. of 1·07–1·13, and only contains 40–55 p.c. of pitch instead of the 60–70 p.c. in tar from horizontal retorts, and also only small amounts of 'free carbon.'

The ammoniacal liquor contains a quantity of ammonia calculated as sulphate, equivalent generally to a yield of from 22 to 30 lbs. of the latter per ton of coal. The composition of ammoniacal liquor and its working up into ammonium salts, are described in the article AMMONIA.

The yield of coke averages about 14 cwts. per ton of coal, but a considerable amount of this is used for heating the retort setting and other purposes on the works, so that the amount available for sale is much less than this, and a sale of 10 cwts. per ton is not often exceeded.

Manufacture of carburetted water gas. In order to obtain a gas of high illuminating power

to mix with the gas from ordinary coal, and increase the illuminating power of the latter, cannel coal was formerly used, rich varieties of which give a gas of as high an illuminating power as 35 or even 40 candles. Owing to the increasing scarcity and cost of cannel, about 1890, recourse was had to oil, as a source of rich gas, this being either carbonised in retorts making oil gas of 60 candle power or higher, or used in the preparation of carburetted water gas, *i.e.* a mixture of water gas and oil gas, which during the previous 20 years had been largely manufactured in the United States, and had, to a large extent, displaced coal gas, and which can readily be made of 20-25 candle power. The carburetted water gas was adopted in a large number of cases, as this plant has the advantage that the volume of gas produced is much greater than with an oil-gas plant, and the apparatus, starting cold, can be put to work in a very short time, and forms a valuable means of quickly increasing the supply in times of sudden great consumption, such as are brought about by fogs or very cold weather. Owing to the now almost general reduction of illuminating power to a quality the ordinary gas coal is capable of yielding, the use of oil gas has been almost entirely given up, but carburetted water gas of an illuminating power similar to that of the coal is made in many undertakings to a large extent, and mixed with the coal gas before storage, about 12 p.c. of the total gas made in

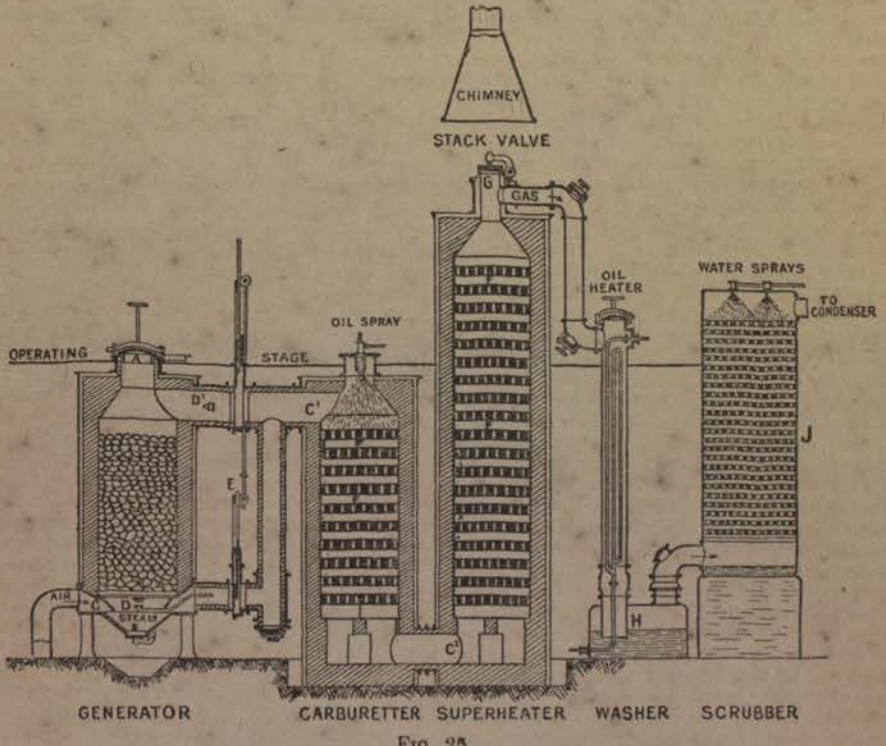


FIG. 25.

the United Kingdom in 1909 consisting of this gas.

The manufacture of water gas itself (commonly known as 'blue' water gas, owing to its burning with a blue non-luminous flame) is dealt with in a separate article (*see* GAS, WATER), and will only be considered here so far as it concerns the manufacture of the carburetted gas. Fig. 25 shows the general arrangement of the Humphreys and Glasgow plant largely employed in the manufacture. The generator A is filled with coke, the latter being ignited at the bottom and raised to incandescence by blowing in air from a fan, the amount of air being regulated so that the gases coming away from the generator contain sufficient carbon monoxide to burn readily. These pass to the top of the 'carburettor' F, which is filled with fire-brick checker work, a secondary stream of air being added to the gas at the top, when the carbon monoxide burns and raises the fire-brick checker work to a red heat. The gases pass away from the bottom and enter the bottom of the 'superheater' G, where they meet with more air, and the remaining carbon monoxide burns to the dioxide, and raises the checker work in the superheater also to a red heat. The waste gases escape into the air from the 'stack-valve' on the top of the superheater, which is open during this operation. When the coke in the generator is sufficiently hot, and the checker work in the carburettor and superheater raised to the required temperature, all three air valves and the stack valve are closed, and steam turned on to the generator, water gas being produced, which passes to the top of the carburettor. At this point oil is sprayed into the gas, and passes with the latter over the

hot checker work, and is first volatilised, the vapours then undergoing decomposition, which is completed in passing through the superheater, the oil being thus converted into permanent gas and condensible tar vapours. The stack valve being now closed, the mixed gas passes through a seal pot, H (which prevents gas returning up the stand pipe when the stack valve is open), thence through scrubbers filled with boards and tubular water-cooled condensers to reduce the gas to atmospheric temperature and condense the tar vapours and excess of steam from the gas. As the formation of water gas takes place with absorption of heat, the temperature of the coke in the generator steadily falls, and eventually reaches a point at which the amount of carbon dioxide produced becomes excessive, and the steam is then shut off, the oil having been also shut off from the carburettor a short time previously; the generator air valve is then again opened, and also the secondary air-valves and stack valve, and the coke and checker work raised to a suitable temperature as before, this period of working being known as the 'blow.' When this is effected, the air and stack valves are again closed, steam and oil turned on, and carburetted water gas made for a further period, known as the 'run,' until the temperature in the generator again falls too low, when steam and oil are again shut off and the blow recommenced. This sequence of operations is then maintained continuously, except during the intervals necessary for adding fresh coke to the generator, and for removing the clinker produced from the ash of the coke. The periods adopted for the length of the blow and run vary somewhat according to the nature of the coke and the available air pressure, a blow and run of 3 and 5 minutes and of 4 and 7 minutes being frequently adopted. The steam supply must be regulated so as not to allow a large excess of undecomposed steam to pass the fuel bed, as in that case a high percentage of carbon dioxide is formed. The checker work temperatures required vary with the class of oil used, the best results being obtained at somewhat different temperatures with different oils, as well as with the quantity of oil used per 1000 cub. ft. of gas made; an average temperature of working is about 750°.

The oil employed is mostly that fraction of petroleum lying between the burning oils and the lubricating oils, frequently termed 'solar' oil, which can be obtained at the lowest price. This is heated before introduction into the carburettor by passing through a coil in the gas main over which hot gas is passing. The amount of oil used depends upon the quality of gas which is desired, and is regulated according to the requirements in this respect.

As the gas production is intermittent, a balancing reservoir is required for the gas if this is to be passed through the purifiers at a uniform rate. For this purpose a relief gas holder is placed at the condenser outlet into which the gas passes intermittently as made, and is drawn from it continuously by an exhauster and forced forward to the purifiers. The gas is purified from tar fog and sulphuretted hydrogen, and from carbon dioxide, if necessary, by the same methods as adopted with coal gas. Usually separate purifiers are employed for this gas, the purified streams of coal gas and carburetted water gas mixing together at the outlet of their respective meters before reaching the holders, but in some cases the crude carburetted water gas is mixed with the coal gas before the purifiers, and the mixed stream purified in the same boxes

The only by-product obtained in the manufacture, other than spent oxide or spent lime from the purifiers, is the oil tar, no ammonia being produced in the process. The oil tar is a comparatively thin oil of sp.gr. 1·0–1·05, consisting mainly of aromatic hydrocarbons. It only contains about 30–35 p.c. of pitch, and scarcely any 'free carbon,' the solid matter found in it consisting chiefly of fine coke ash carried over from the generator with the stream of water gas. It is mostly sold to distillers, but is sometimes used as fuel, and also for washing the crude coal gas to remove naphthalene, of which it normally contains only small amounts. Sometimes the tar separates as an emulsion with water, from which the latter only separates with great difficulty.

The amount of coke employed in the manufacture, including that used for raising steam, amounts to from 40 to 50 lbs. per 1000 cub. ft. made, whilst the consumption of oil varies considerably, according to the quality of gas required. With good working each gallon of oil of good quality used per 1000 cubic feet will give an illuminating power of 7–8 candles if the carbon dioxide is removed. The quantity of oil tar produced amounts to 12–15 p.c. of the oil used.

Carburetted water gas contains the same constituents as coal gas, but their relative amounts differ considerably, the percentages of carbon monoxide and ethylene being higher, and those of hydrogen and methane lower; it only contains small amounts of sulphur compounds other than sulphuretted hydrogen.

The following analyses of coal gas, carburetted water gas, and of a mixed gas containing about 20 p.c. of the latter, are fairly typical, and show the general character of the difference:—

	Coal gas	Carb. water gas	Mixed gas
Carbon dioxide .	1·2	3·8	1·6
Ethylene and benzene	3·2	11·4	4·1
Oxygen . .	0·4	0·2	0·5
Carbon monoxide	9·1	31·0	12·2
Methane . .	30·2	15·0	28·1
Hydrogen . .	48·5	32·9	46·2
Nitrogen . .	7·4	5·7	7·3

Carburetted water gas usually contains small amounts of ethane as well as methane.

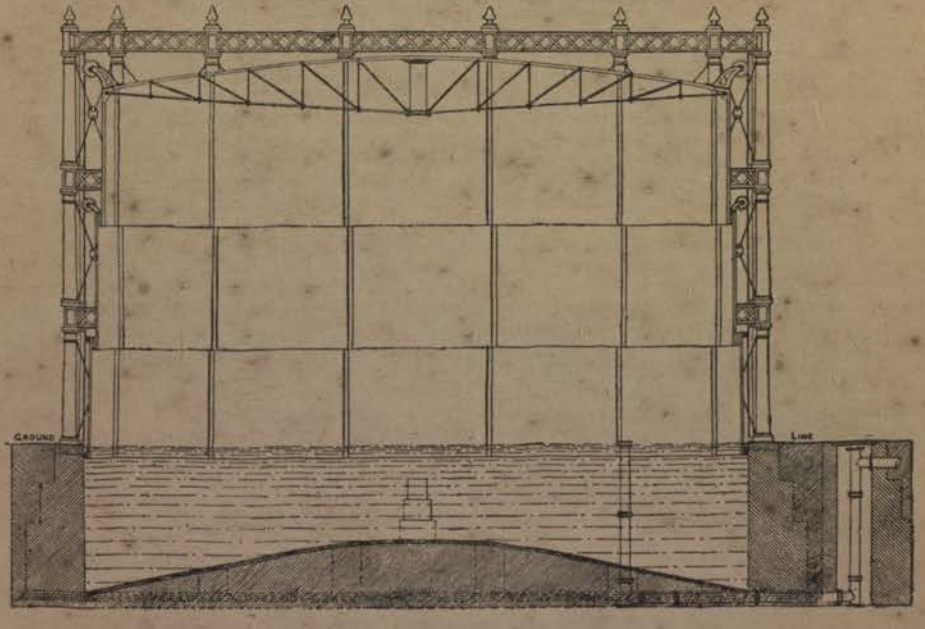
The sp.gr. of carburetted water gas is much higher than that of coal gas of the same illuminating power, owing especially to its smaller percentage of hydrogen. It varies considerably, according to the percentage of oil gas in it, but usually falls within the limits of 0·6 and 0·75 (air = 1).

Measurement, storage, and distribution of the gas. The gas, leaving the purifiers, passes to the station meters in which its volume is measured, and thence to the gas holders, where it is stored ready for distribution as required. The meters employed are usually wet meters, similar to those used as consumers' meters, but of very much larger size. The temperature of the gas passing and the height of the bar is noted, and

the volume recorded by the meter corrected to standard temperature and pressure, which is, however, not the 0° and 760 mm. barometer employed for scientific purposes, but that of the gas at 60°F. and 30 inches bar. saturated with moisture, this being approximately the average condition of the gas when sold to consumers, whose payment is made by volume.

The gas holders (Fig. 26), consisting of a large bell with suitable guide framing floating in a tank of water, are often of very large size, the largest being capable of holding about 15,000,000 cub. ft. In order to reduce the necessary depth of the tank, the bell is usually constructed in a number of lifts which slide into each other in a somewhat similar manner to the cylinders of a telescope. The weight of the holder keeps the gas within it under a pressure equivalent generally to the weight of a water column of 4–10 inches, according to the weight and diameter of the holder.

In order to control the pressure of the gas in the mains on the district of supply, a governor is fixed between the holder and the trunk mains, whereby the pressure in the distribution mains is reduced to that most suitable, after which it is automatically maintained at that pressure. Fig. 27 gives a section of a governor in frequent use. The gas, entering in the direction shown by the arrows, must, in order to reach the outlet, pass through a device, consisting of a hollow vertical cylinder closed at the top and having a number of slots cut in the vertical side, the width of which increases towards the top of the



— SECTION THROUGH TANK AND GASHOLDER —

FIG. 26.

cylinder. The top of this cylinder is connected by a rod with the bell above, and is capable of moving freely up and down with this bell which is sealed in water. When water is allowed to run into the annular chamber in the bell, the latter increases in weight, and with the attached cylindrical device sinks, increasing the size of the openings through which the gas can pass, and by adjustment of the amount of water the desired pressure at the outlet can be obtained. If, then, owing to increased consumption, the pressure of the gas in the outlet main falls, this lessened pressure is transmitted to the bell, which, under the atmospheric pressure, falls, increasing the size of the gas openings, allowing more gas to pass and restoring the pressure in the outlet main. If the consumption decreases and pressure increases, the bell rises and reduces the size of the gas openings, and in this manner the pressure once set remains constant. When it is desired to alter the pressure in the outlet main to allow for the periods of higher or lower consumption on the district, water is either added to or run off from the annular chamber in the bell.

Formerly the holders gave more pressure than was required on the district, but at the present time, owing to the greater consumption and the higher pressures which are required for the efficient working of incandescent burners, gas fires and gas engines, it frequently happens, especially in large works, that the pressure given by the smaller holders and the upper lifts of the larger ones is insufficient. In such cases the gas is drawn from the holder by means of fans, and forced forward at higher pressure to the works governor, or carried into the district by separate high-pressure mains, the gas from which is passed into the ordinary distribution mains at suitable points for maintaining good

and uniform pressure throughout the area of supply.

Calorific power, illuminating power, and purity of gas. With the exception of a few small private gas works, the whole of the gas undertakings in the United Kingdom, whether in the hands of companies or local authorities, are subject to the general conditions laid down in the Gas Works Clauses Act, 1871, and also to special conditions defined in separate Acts

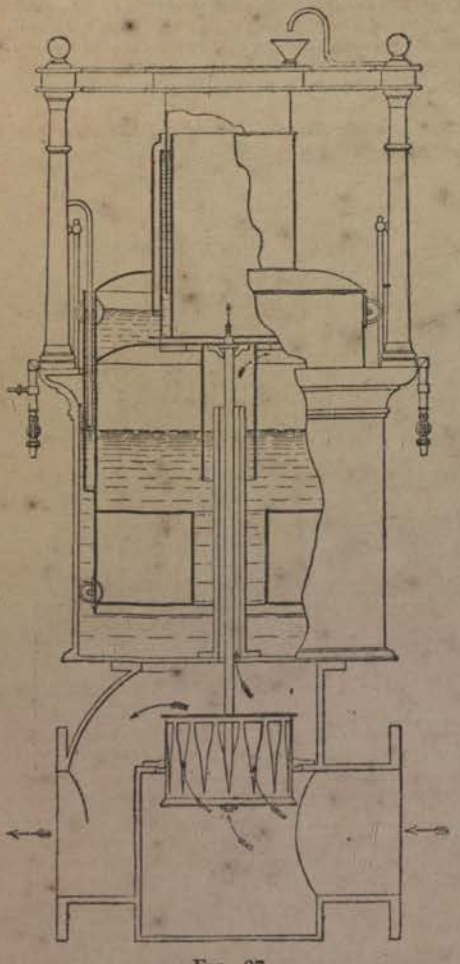


FIG. 27.

relating to each particular undertaking, such Acts defining, amongst other matters, the minimum illuminating power and the minimum pressure which must be maintained, and the maximum amount of certain impurities which may be present in the gas.

With respect to purity, the only stipulation mostly made is in respect of sulphuretted hydrogen, the stipulation being that the gas, when passed for 3 minutes at the rate of 5 cub. ft. per hour, over bibulous paper moistened with lead acetate solution, shall not darken the paper, owing to formation of lead sulphide. As the formation of a brown stain in this manner is an exceptionally delicate test for sulphuretted hydrogen, this means that for all practical purposes the gas passing the test is free from that impurity. The stipulations formerly existing in many undertakings with regard to the amount of sulphur in the gas in forms other than sulphuretted hydrogen, have now, in almost every case, been repealed, and the same is the case with regard to ammonia, for which a limit of 4 grains per 100 cub. ft. was formerly sometimes given, the amount actually found in the gas supplied being now almost always far below this limit. With respect to pressure, the stipulations as to which date from the time when gas was mainly used in flat flame burners, the usual requirement is that the minimum pressure from midnight to sunset shall be equal to a column of water $\frac{6}{10}$ inch in height and to one of 1 inch from sunset to midnight. Such pressures would be absolutely useless with the apparatus in which the gas is at present used, and it is now always supplied at much higher pressure, the general aim being to so arrange matters that the pressure throughout the district of supply never falls below 2 inches.

With regard to quality, except in the case of one undertaking, the only stipulation made is with regard to the minimum illuminating power which must be maintained, the exact quality specified being separately laid down for each undertaking, and varying considerably in different parts of the country, the number of candles per 5 cub. ft. an hour mostly varying from 13 to 20 in England and Ireland, whilst in Scotland qualities of 25 candles or more are sometimes supplied. Under present day conditions, however, probably not more than 10 p.c. of the gas is burned in open-flame burners, the remainder being burned in incandescent burners, gas fires, gas cookers, gas engines, and in Bunsen burners for other industrial purposes, and the illuminating power of the gas is of but little value for representing the comparative value of the gas for such uses. For these, the property of primary importance is its calorific power, *i.e.* the number of heat units evolved by the complete combustion of a definite volume of the gas.

The calorific power of a gas is an absolute value, being, in fact, the total potential energy of the gas expressed in heat units, but the illuminating power has no absolute value, being dependent on the construction of the burner and on the rate at which the gas is burned. There is, therefore, no definite constant relation between the calorific and illuminating power, and it is possible to obtain a gas of very high calorific power which has little or no illuminating power, and a gas of high illuminating power which is of low calorific power. Thus, for example, methane burns with only a slightly luminous flame, but has a very high calorific power, whilst a mixture of hydrogen and sufficient benzene vapour has a high illuminating power, but low calorific power. With illuminating gas, as generally manufactured, the composition of which only varies within certain limits, it is found that in most cases the illuminating power and calorific power do, on the average, rise and fall together, but the rate of rise and fall of the latter takes place at a much slower rate than that of the illuminating power. A reduction of the illuminating

power is therefore accompanied by a much smaller reduction of calorific power, and the tendency of legislation has been to reduce the minimum illuminating power specified for the different undertakings, which has, to some extent, adjusted matters to suit modern requirements. In Germany, on the other hand, and to a less extent in other continental countries, the illuminating power standard has been almost entirely abandoned in favour of working to a calorific standard, and the gas there supplied has frequently only an illuminating power, tested under the most favourable conditions, of 10 candles or less, whilst the calorific power is the same as that supplied generally in the greater part of England.

It must, however, be remembered that, although the calorific power of the gas is of very great importance, it is not the only factor to be considered. The efficiency of the apparatus in which the gas is used depends, in most cases, not only on the amount of heat liberated, but also on the temperature of the flame produced. The presence of large quantities of incombustible gases, such as nitrogen and carbon dioxide, lowers the flame temperature to a greater extent than the calorific power, and, although their presence cannot be altogether avoided, it is desirable that their amount should be kept as low as possible, consistently with economic working of the manufacturing process in other respects. Further, the average flame temperature in burners of the Bunsen type, by which most of the gas is now consumed, varies greatly according to the volume of primary air drawn into the burner by the injecting action of the gas jet issuing from the burner nozzle, as the most suitable proportion depends upon the composition of the gas, and the actual amount drawn in varies according to both the pressure and the sp.gr. of the gas; if, therefore, the apparatus is set to give the greatest efficiency under certain conditions of pressure, composition and sp.gr. of the gas, this efficiency will not be maintained if the gas undergoes considerable variations in any or all of these points. From the consumer's point of view, therefore, better results ensue from the

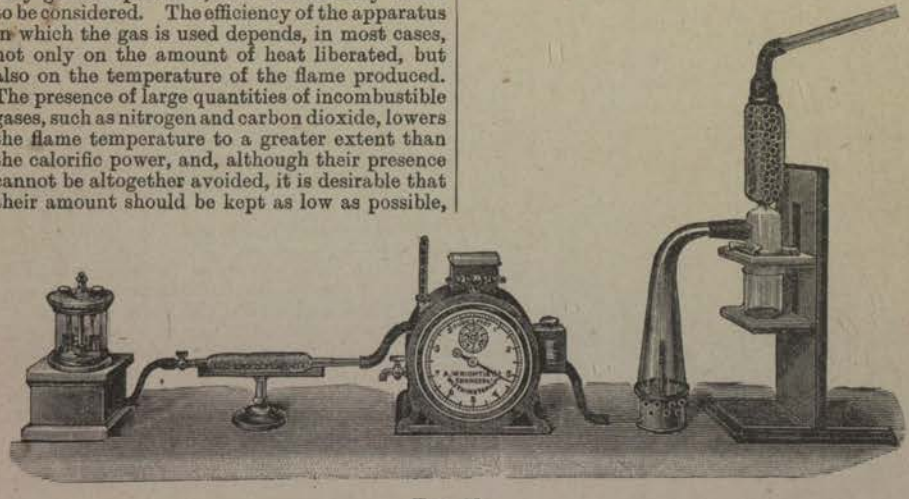


FIG. 28.

supply of a gas of fairly uniform, although lower average calorific power, with reasonable constancy of pressure, composition, and sp.gr., than with gas of much higher average calorific power, which is subject to great fluctuations. Whilst it is not practicable to obtain exact uniformity of calorific power, composition, and sp.gr., and also of pressure throughout a large area of supply, except at a cost which would be prohibitive, this end ought always to be aimed at so far as it can be effected with reasonable economy.

Determination of total sulphur. The official method for estimation of the total sulphur present in purified gas is that prescribed by the Metropolitan Gas Referees, which is illustrated in Fig. 28. The gas, if it is also to be tested for sulphuretted hydrogen and ammonia, is passed first over test papers made by soaking blotting paper in a 10 p.c. solution of lead acetate, and exposing such slips, whilst damp, to an atmosphere containing ammonia, and then over a cylinder filled with glass beads or broken glass, moistened with a known volume of standard sulphuric acid, to remove ammonia. It is then burned in a small Bunsen burner at the rate of 0·5–0·7 cub. ft. per hour until 10 cub. ft. have passed, the flame being surrounded by lumps of commercial ammonium carbonate. The products of combustion, together with ammonia, pass by means of the trumpet tube into the glass cylinders provided with a tubulus at the bottom for connecting with the trumpet tube; the upper portion of the cylinder is filled up with glass marbles, and from the top a wide bent-glass tube is led, which acts as a chimney and final condenser. A small tube drawn out to a jet conveys the condensed products to a flask or beaker placed on a shelf below. The sulphur dioxide formed by the combustion of the sulphur condenses in presence of the moisture, excess of oxygen and ammonia forming a solution of ammonium sulphate, and when the required amount of gas has been burned, the cylinder is washed out with water, and the sulphur present in the liquor estimated as barium sulphate in the usual manner, the amount being calculated as grains of sulphur per 100 feet. This method tends to give slightly low results, as the sulphurous acid primarily formed is not always completely oxidised to sulphuric acid, and escapes precipitation with barium chloride, on which account many prefer a previous treatment of the solution with bromine, or

precipitation with nitric acid and barium nitrate. The sulphur estimation may also be made by aspirating the products of combustion through wash bottles containing sodium hypobromite solution, and subsequent precipitation of barium sulphate, or through neutral hydrogen peroxide, the sulphuric acid produced in the latter case being determined by titration with standard alkali.

Determination of calorific power. Several calorimeters are in use for this purpose, all of which are in principle indentical with the form proposed by Hartley (J. Gas Lighting, 1884, 1142), the gas being burned at a constant rate in a chamber through which water also flows at a constant rate. The instrument in most frequent use in all parts of the world is the Junkers' calorimeter, a section of which is given in Fig. 29.

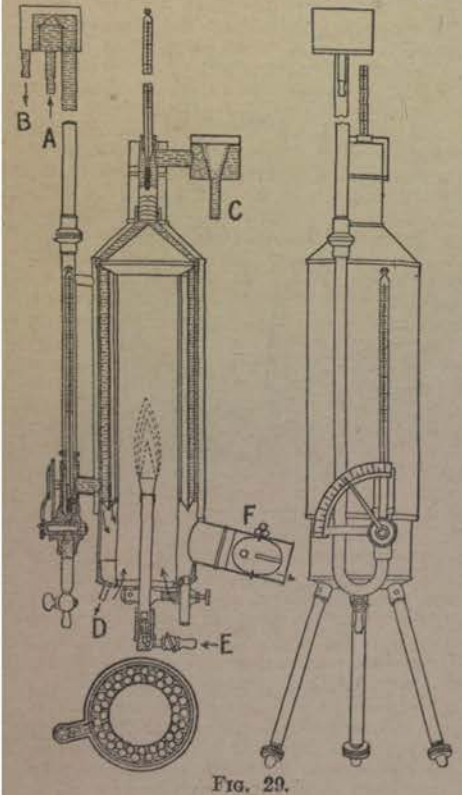


FIG. 29.

The gas, after passing through a governor and meter, is burned in a large Bunsen burner, E, in the central portion of an annular copper chamber, the annular space of which is traversed by a large number of copper tubes down which the products of combustion pass and escape into the atmosphere by the side opening F, which is provided with a damper regulating the amount of air passing through the apparatus. The water is run into the upper small reservoir A, provided with an outlet proper to the calorimeter, and a constant level overflow B, the rate at which the water enters being maintained above that passing through the calorimeter, the excess passing away by the overflow, thus maintaining a constant head of water. The water flows down, past the regulating cock and inlet thermometer, to the bottom of the annular chamber, and flows upwards to the top around the tubes conveying the products of combustion in the reverse direction, and cools the latter to the temperature of the incoming water. The water leaves the annular chamber at the top and passes through a series of baffle plates to ensure thorough mixing, over the outlet thermometer to the overflow funnel C. The water condensed from the gas collects at the bottom of the annular chamber and flows out through a small tube into a collecting cylinder.

The gas and water supplies are adjusted so that the difference in the readings of the inlet and outlet water thermometers is 10°–15°, and when equilibrium is attained and the condensed water is also dripping regularly from the small tube, D, at the bottom of the calorimeter, the water from the calorimeter is diverted into a collecting vessel as the meter hand passes a point which is noted, and a small measuring cylinder placed to collect the condensed water. Frequent readings of the inlet and outlet thermometers are made, until a sufficient amount of water has been collected (from 2 to 5 litres are mostly taken); to conclude the test, the gas may be shut off when the collecting vessel is filled to a definite point, or the water may be diverted from the measuring vessel as the meter hand passes a noted point. The volume of gas is taken from the meter readings and corrected to that of the moist gas at 60°F. and 30 inches bar., the weight of water passed determined by measurement or by weighing, and the average increase in temperature of the water found from the readings taken during the test. The calorific power of 1 cub. ft. of the gas, expressed in large calories, is equal to:

$$\frac{\text{weight of water in kilos.} \times \text{temperature C.}^{\circ}}{\text{volume of gas consumed}}.$$

In this country the value is usually expressed in British thermal units, *i.e.* the amount of heat required to raise 1 lb. of water 1°F., each calorie being equal to 3·968 B.Th.U., and to obtain the result in these units the number of calories found must be multiplied by that factor.

The calorific value thus obtained includes the latent heat evolved by the condensation of the steam produced by the combustion of the hydrogen contained in the gas, and is termed the *gross* calorific power. In almost all the practical applications of gas, the products of combustion pass away at temperatures above which the condensation of the steam occurs, so that this latent heat cannot be utilised either for the production of high temperature in the flame of the burning gas, or for development of power in the cylinder of a gas engine. A deduction of this amount of latent heat is therefore made from the gross calorific power, the difference, excluding this heat, being termed the *net* calorific power. The amount of such latent heat is ascertained by collecting the condensed water which flows from the calorimeter during the test, a larger volume of gas than that required for the determination of the gross value being burned for this determination (about 1 cub. ft.). Each c.c. of water evolves, in condensation, 0·536 cal., and the amount to be

deducted is found by multiplying 0·536 by the number of c.c. of condensed water per cub. foot of gas burned. The usual practice is, however, to deduct 0·6 cal. for each c.c. of condensed water, this representing not only the latent heat, but also the sensible heat lost by the condensed steam in cooling from 100° to atmospheric temperature, and the 'net' figures then obtained are rather lower than the true net value, which has to be employed in thermodynamic calculations.

The Simmance-Abady calorimeter is a modification of the original Hartley calorimeter, and the method of working corresponds closely to that described for the Junkers calorimeter. In

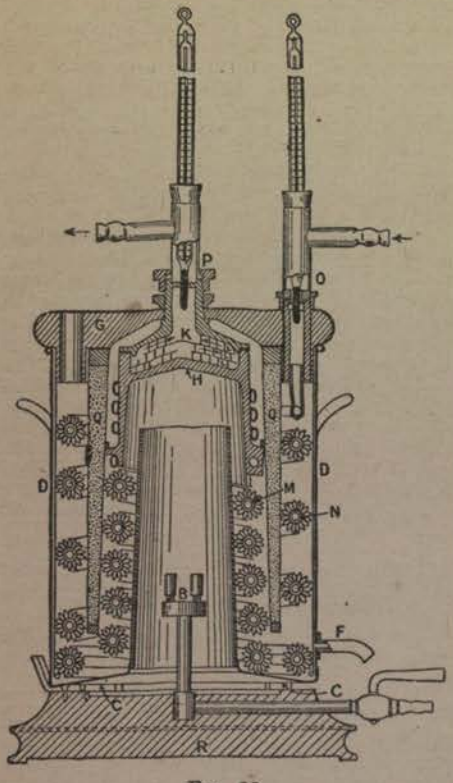


FIG. 30.

this instrument the products of combustion, instead of passing through tubes, travel downwards through a series of annular chambers separated by similar chambers up which the water flows. The Boys calorimeter, prescribed by the Metropolitan Gas Referees for use in official calorific power tests in London, is shown in section in Fig. 30. The base R carries the pair of union jet burners B, which are supplied with the gas to be tested through a governor and meter; the calorimeter vessel proper D, after lighting the gas, is then placed in position over the flame, and rests on three centering and lifting plates C, leaving a space through which the air required for combustion enters. The products pass up the copper chimney and thence into the annular space between the chimney and the outer side of the calorimeter vessel. This annular space is divided into two portions by a brattice of thin sheet brass filled with non-conducting material such as cork-dust, which causes the combustion products to pass first down the inner portion of the annular space, and then up on the outer side to the top, where they escape into the atmosphere through holes bored in the wooden top. A tube of copper, to the outside of which is sweated a helix of copper wire, giving it a large conducting surface, is led in a spiral, first from top to bottom of the outer annular chamber, then around the bottom below the brattice, and finally up the inner annular chamber. The water is led over the inlet thermometer through this tube, passing first through the outer annular chamber, then along the bottom, into which water is placed before commencing a test, and up the inner annular chamber, and in its travel absorbs the heat of the products of combustion. Before reaching the outlet thermometer, the water passes through the central temperature-equalising chamber.

The general method of working is similar to that of the Junkers calorimeter, full details of construction and working being given in the official notification of the Gas Referees (Wyman and Sons, Ltd.). (For details of the necessary precautions to obtain accurate results in gas calorimetry, *see* J. Gas Lighting, 1908, 104, 904; Coste, J. Soc. Chem. Ind. 1909, 28, 1231.)

The gross calorific power of the gas now supplied varies in different parts of the country, for the most parts between the limits of about 550–650 B.Th.U. gross per cub. ft., and in the majority of cases falls between 550–600 B.Th.U. gross, the net calorific power being about 10 p.c. below the gross value. Carburetted water gas has a lower calorific power than coal gas of the same illuminating power, the gross figure approximating to 15 p.c., and the net figure to 10 p.c. lower than the corresponding coal-gas figures.

Determination of illuminating power. The apparatus for the determination of illuminating power consists of three essential parts: (1) a standard source of light; (2) a burner in which the gas can be burned under definite conditions; (3) apparatus for accurately measuring the distances at which the standard and gas flames effect equal illumination, the relative intensities of the two sources of light being, in accordance with the law of inverse squares, proportional to the square of their distances from the illuminated surface under these conditions.

The standard of light in Great Britain and Ireland is defined by the London Gas Act of 1860, as that given by 'sperm candles six to the lb., each burning 120 grains per hour,' and such candles were formerly used, in most cases, in the determination of illuminating power. These are, however, a most unsatisfactory standard, and have now been largely replaced by the 10-candle pentane lamp, devised by Prof. A. Vernon Harcourt, the Senior Metropolitan Gas Referee. Candles are, however, still employed in many cases, as, unfortunately, the general Act of Parliament of 1871, controlling gas undertakings, specifies their use and remains unaltered, and only those undertakings which have obtained special clauses in their separate Acts

for the purpose can legally use the 10-candle standard.

The Harcourt 10-candle lamp is illustrated in Fig. 31. Air is admitted to the saturator at the top of the apparatus two-thirds full of pentane, and passes in a zigzag course over its surface by the cock S_1 becoming saturated with the vapour, and thereby heavier than air. The heavy gas falls through S_2 down the rubber connecting tube to the argand B, where it burns with a highly luminous flame. The latter is drawn into

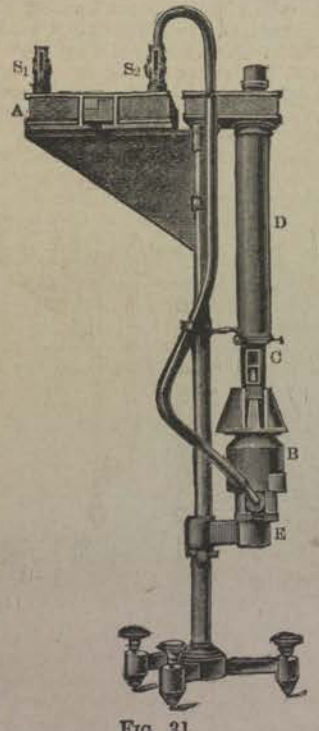


FIG. 31.

form by the inner brass chimney C, 30 mm. in diameter, the lower end of which is fixed exactly 47 mm. above the steatite ring of the burner when the lamp is cold. The supply of mixed gas to the flame is regulated so that the average tip, as seen through the mica window in the metal chimney, is half-way between the bottom of the window and the cross bar on the window. Under these conditions, with the top of the flame screened off, the amount of light emitted from the exposed portions is equivalent to 10 standard sperm candles, and the amount of light emitted from the unscreened portion is not affected materially by slight variations in the total height of the flame. Around the inner chimney is a wider one, D, open at the bottom, the air entering the annular space there, becomes heated, and travels down the hollow central support of the lamp to the centre of the flame.

The pentane employed (which consists chiefly of *iso*pentane) is obtained by the fractional distillation of light American petroleum, and should have a sp.gr. at 15° of not less than 0·6235, or more than 0·626, compared with water at 4°, and a vapour density of between 36 and 38 compared with hydrogen. Hydrocarbons of other groups, *e.g.* olefines and benzenes, must be absent.

The standard burner. It has been mentioned that the illuminating power of a gas has no absolute value, but varies with the construction of the burner, and the rate at which the gas is burned, and it is therefore necessary to define the conditions in these respects closely. Unfortunately, very different definitions have been adopted for different undertakings, which have rendered almost impossible any comparison of the results obtained in different parts of the country, as a gas testing, say, 16 candles in one town, may really be lower than one testing 14 candles in another, owing to differences in the burner used. The exact type of burner to be used has, on this account, led to a very acute controversy, which lasted many years, but at the present time this has been practically settled by the adoption of Carpenter's Metropolitan No. 2 argand burner, which enables gases of widely different quality, up to about 20 candles, to be tested under conditions which in all cases give fairly truly the relative illuminating power. This burner consists of a specially constructed argand burner, its characteristic feature being the provision of a damper below the burner, which allows of an adjustment of the volume of air entering the burner on each side of the annular gas flame. The gas is burned at the rate of 5 cub. ft. per hour, and the damper adjusted until the flame is just short of smoking, at which point the light emitted is the maximum that can be obtained from the gas in that burner. This burner is now adopted in the Metropolis and a large number of provincial undertakings, and although many other burners are still in use, powers to substitute the Metropolitan No. 2 argand are usually obtained when any gas undertakings come to Parliament for new powers, and its use will probably soon be universal.

Bar photometer. In determining the illuminating power, the bar photometer is the instrument in most frequent use; in this the Harcourt 10-candle standard or candles, and the standard burner, are fixed at opposite ends of a bar, in such a manner that the top of each burner is the same height above the table, and the centre of the two flames exactly 60 inches apart. The apparatus is provided with the necessary gas-meter, governor and adjusting cock for regulating the rate of consumption and maintaining it constant, and a stop clock or watch for timing the meter. Suitable screens are also provided to prevent the light from the flames, other than that coming from the disc box, reaching the eye of the observer, and also to protect the flames from draughts. Fig. 32 represents a form of bar photometer in frequent use, which clearly shows the general arrangement.

In order to determine the distances at which the two lights effect equal illumination, the Bunsen disc is most commonly employed in this country. This consists of a piece of white paper, which, with the exception of a circular spot in the centre, is made translucent by painting with a solution of spermaceti in benzene. The paper is fixed in a suitable box having a blackened interior, in such a manner that the

plane of the paper is vertical and at right angles to the direction of the bar. The box itself is fixed on a carriage which can be moved along the bar in either direction, the height of the box being such that the centre of the disc is in line with the central axis of each flame, and the same height as the bottom of the burners. By means of mirrors placed at the back of the disc box, the observer is enabled to view both sides of the disc simultaneously, and, by moving the disc carriage along the bar, can find the point at which the unpainted spot nearly disappears, and especially the point at which the boundary line between the painted and unpainted spot appears to be exactly similar on each side, this being the point of equal illumination.

When the Harcourt lamp has been burning 15 minutes, and the height of the flame correctly adjusted, and the rate of gas consumption also regulated to 5 cub. ft. per hour, the damper on the argand is slowly closed until the flame is just short of smoking. The disc box is then moved backwards and forwards until the point of equal illumination is found, four readings being usually taken. The bar is graduated so that the illuminating power is directly read off, avoiding the necessity of measuring the exact distances and squaring these, and a correction made for the temperature of the gas and the height of the barometer, the results being given as the number of candle illumination yielded by the gas when burned at the rate of 5 cub. ft. per hour, and saturated with moisture at 60°F. and 30-inch bar.

In Germany the Lummer-Brodhun disc box is mostly used, in which the light from the two sources falls on two pure white surfaces, each of which can be simultaneously viewed by a telescope through a system of prisms. Both this and the Bunsen disc have the objection that when the two sources of light have different colours, such as occurs in the testing of incandescent burners against a pentane standard, the point of equality of illumination is not

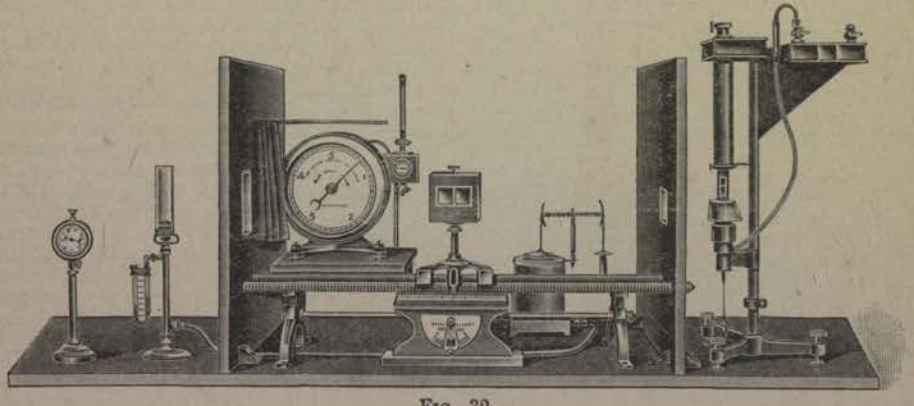


FIG. 32.

readily acsertained. In such cases the *flicker photometer head* (*see* Simmance and Abady, Proc. Phys. Soc. 19, 39) is largely used, in which reflections of each source of light are alternately transmitted to the observer in rapid succession by means of a specially constructed rotating white disc actuated by clockwork; so long as the light from each source is unequal, a flickering effect is noticed, but this ceases as soon as equality of illumination is obtained, irrespective of the colours of the sources of light.

Table photometer. In this form of photometer, adopted by the Metropolitan Gas Referees for official illuminating power tests in the Metropolitan area, the pentane standard and argand burner are so arranged that the light from each source passes through an oblong hole in a screen on to a sheet of translucent white paper free from water marks, thus illuminating two adjacent portions of the paper which just touch each other without overlapping. The 10-candle standard is always at the fixed distance of 1 metre from the photoped carrying the translucent paper, and the observer from a position on the opposite side of the paper to the sources of light is able to increase or decrease the distance of the gas burner from the screen, until the two lighted portions of the paper appear equally illuminated. Full descriptions of the table photometer and of the 10-candle pentane standard are given in the Metropolitan Gas Referees' Notification (Wyman & Sons).

The room in which the photometrical measurements are carried out should be of ample size, and, whilst free from draughts, should have thoroughly efficient ventilation if correct results are to be obtained. The temperature should be kept as uniform as possible, and, in particular, should not fall much below 15°, in which case the results may come out much below the true value.

In addition, photometrical observations are also required for other purposes, such as the illuminating power of gas in incandescent burners, the amount of light emitted by the various burners at different angles, and the actual illumination of indoor and outdoor surfaces. Space will not allow of the consideration here of the somewhat complicated apparatus necessary for these applications.

Development of light from gas. In the practical employment of gas for illumination purposes, the only method formerly known was the combustion of the gas in open flames in the air; the actual union of the gas and air only takes place in the outer surface of the flame in a thin film, where a very high temperature is developed, and the action of the heat thus

evolved on the unburnt gas within the flame effects its thermal decomposition, and results in the production of solid particles within the flame, consisting of dense hydrocarbons and free carbon, which are then raised to incandescence before undergoing combustion and emit light, the light being whiter and brighter the higher the temperature of the flame.

The great majority of such open-flame burners are those in which the gas is made to issue from the nipple in a thin flat flame, two types of such burners being in common use. In the first type, known as the fishtail or union jet (Fig. 33), the gas issues from two holes in the nipple inclined to each other as shown, which, on meeting, coalesce to a flat flame at right angles to a plane passing through the two orifices, the size of these being regulated according to the amount of gas it is desired to consume and also to the quality of the gas. Such burners are relatively fairly efficient with rich gases, but are totally unsuited to the quality of gas now usually supplied, although, owing to their cheapness, they are still largely used. They tend to draw a certain amount of air into the flame, and whereas with rich gases the temperature of the flame is thereby raised and the production of a smoky flame also prevented, the effect with gas of low illuminating power is that much of the hydrocarbon content of the

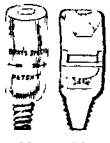


FIG. 33.

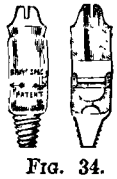


FIG. 34.

gas is directly burned without any separation of carbon, this resulting in much loss of illuminating power. The second type of burner, the batswing or slit burner (Fig. 34), has a dome-shaped top through which a narrow slit is cut. The width of this slit is varied according to the quality of the gas for which it is required, the lower the illuminating power of the latter, the greater being the width of slit necessary to give the best results.

In all flat-flame burners the pressure of the gas at the burner nipple must be slight, so that the gas issues at low velocity, as, when the velocity exceeds a certain limit, the flame becomes noisy and irregular, and air is drawn into the flame, reducing the amount of carbon formed and the light emitted for a given consumption of gas. To avoid this, the stalk of the burner is usually partly blocked by suitable stuffing, so as only to allow about the requisite amount of gas to pass under the pressure usually available, or each burner may be provided with a simple governor, as shown in Fig. 35.

The actual illuminating power obtained with such burners varies very greatly; with good types in proper condition, the light obtained with gas of the quality now mostly supplied is from 2·5 to 3 candles per cub. foot of gas consumed per hour, but with unsuitable types which are also dirty and neglected, the light often falls below 1 candle under the same conditions. The use of such burners has, however, steadily decreased since the introduction of the incandescent burner, and, except in certain factories where the employment of the latter is attended with difficulty, they are now mainly employed in places, such as passages, where but little illumination is required, or in rooms which are only occasionally used, and the actual amount of gas burned in such burners is a constantly decreasing quantity, and is probably in most cases below 10 p.c. of the total consumption.

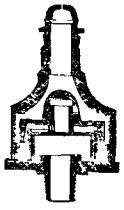


FIG. 35.

The argand burners, in which the gas is burned in an annular flame surrounded by a glass chimney, which draws a current of air both along the external and internal surface of the annular flame, give a higher efficiency, amounting with common gas to 3–3·5 candles per cub. ft. Still higher efficiency is obtained with the regenerative burners, in which the waste heat of the products of combustion is utilised to heat both the gas and air before they undergo combustion. These types of burner have, however, been almost completely superseded by the still more efficient incandescent burner.

In these last, the development of light is obtained by raising to incandescence a mantle composed essentially of thoria, to which about 1 p.c. of ceria has been added. The manufacture of these mantles is dealt with in a separate article (*see* GAS MANTLES). In order to raise such mantles to incandescence, the gas is burned in a non-luminous flame of the Bunsen type, by mixing with the gas a certain proportion of primary air before it undergoes combustion, when it burns with the well-known non-luminous flame, having a definite two-coned structure.

Whilst the actual causes of the high development of light from such a mantle are still a matter of dispute, there is no question that the amount of light emitted increases greatly with the temperature to which the mantle is raised. In order, therefore, to obtain the highest practical efficiency with such burners, the gas must be burned in such a manner as to produce a flame of high temperature, and this must also have such a shape that the mantle is situated in the zone of highest temperature.

The effect of the introduction of the primary air to the gas before combustion is that in the flame the gas first undergoes combustion with the limited amount of oxygen present in it, yielding a mixture of steam, carbon dioxide, hydrogen, and carbon monoxide, together with the nitrogen of the added air, this reaction taking place in the area visible as the ' inner cone,' all hydrocarbons completely disappearing from the gas, provided the amount of oxygen in the mixed gas undergoing combustion is rather more than half that required for its complete oxidation. This mixture of ' water gas ' and nitrogen forms the ' outer cone ' of the flame, which has itself been raised to a very high temperature by the reactions occurring in the inner cone, and the hydrogen and carbon monoxide then burn where the air is in contact with the outer cone, further increasing the temperature at this surface, and the relative shape of flame and mantle should be so arranged that the latter occupies as-

nearly as possible the zone in which this final oxidation is taking place.

The higher the proportion of primary air added, the smaller is the size of the flame, and especially of the inner cone, and the higher the average temperature of the flame, the highest efficiency of an incandescent burner being obtained when the amount of primary air added is equal to that theoretically required for the complete combustion of the gas. Under ordinary conditions of gas supply, however, this condition cannot be obtained, as a mixture of gas with the full amount of air is highly explosive and the explosion wave travels back from the flame at a velocity greater than that of the advancing mixture of gases, and the burner 'fires back,' the gas then igniting at the injector nozzle. Under ordinary conditions, it is not practicable to admit as primary air more than about three-fifths to four-fifths of the total amount required for complete combustion. On the other hand, if the proportion of primary air admitted is too low, the hydrocarbons of the gas are not completely converted into water gas in the inner cone, some hydrocarbons passing to the outer cone, in which case, apart from the lower temperature of the flame produced, carbon may be deposited on the mantle, which becomes blackened, and its light emission thereby greatly reduced.

The proportion of primary air drawn in through the air holes of the burner, depends, not only on the construction of the latter, but also to a very large extent on the pressure of the gas and its specific gravity. The higher the pressure of the gas, and the lower its specific gravity, the smaller is the opening which is necessary for the passage of the required amount of gas, and the higher its velocity, and it is largely the latter factor which determines the amount of air sucked in through the air holes. On this account the pressure at which the gas must now be supplied is much higher than was necessary for flat-flame burners, and should be equal to that of a water column at least 2 inches in height; with lower pressures, especially with higher qualities of gas, it is much more difficult to get a well-aërated flame, and to avoid the deposition of carbon on the mantles.

With the upright incandescent burners, first introduced and still largely in use, the flame burns from the top of the burner. The central portion of the burner head is solid, so that the flame produced is annular, the central closed portion having a socket in which is placed the fire-clay crutch supporting the mantle, and the annular space covered with wire gauze or similar device to prevent 'flashing back.' To obtain a good efficiency, the size of the gas nozzle and air holes of the burner must be adjusted so that, under the average pressure existing at the burner, a well-aërated flame is produced, having only a small inner cone, and of such a size that the mantle, when put on, lies fully in the zone of highest temperature. When adjusted to give the best results, an efficiency of 25–30 candles can be obtained, although, as the mantle ages, this tends to fall off, largely owing to alterations in shape of the mantle, which cause portions of it to occupy positions of lower temperature in the flame. Periodic cleaning of the burner is also necessary, as the dust in the air drawn in tends to settle on the gas nozzle and on the wire gauze of the burner head, and results in less air being drawn in and the production of an under-aërated flame of lower temperature.

In the inverted incandescent burner, which is now largely replacing the upright burner, the flame is directed downwards, the mouth of the burner being in this case fully open, and the mantle supported from above on a ring of fire-resisting material attached to the burner, this form possessing the great advantage that no shadows are thrown on the surfaces below, which are in most cases those which it is specially desired to illuminate. The proper adjustment of gas and air supplies, and a sufficient gas pressure, as well as the periodic cleaning of the burners from dust, is equally necessary with the inverted form, but when working under the most favourable conditions, these are more efficient than the upright burners, over 40 candles per cub. ft. having been obtained using gas of the quality and at the pressure common in the south.

By considerably increasing the pressure at which the gas is supplied, namely, to one equal to a column of about 55 inches of water or higher, much higher efficiencies are obtained, both with the upright and with the inverted burners. With the increased pressure, the velocity at which the gas can be made to issue from the injector nozzle is so increased, that the full amount of air necessary for its combustion can be drawn in through the air holes, and the mixture forced with much higher velocity through the burner, so that the tendency of the flame to flash back through the highly explosive mixture can be controlled, and a flame of very high temperature produced, resulting in a much greater light emission from the mantle on which the flame acts. With such high-pressure burners, efficiencies of as high as 70 candles per cub. ft. are obtained. High-pressure installations are now very largely adopted for outside lighting of the public streets and yards, and also for interior lighting in workshops and large public buildings, special plant being usually erected for compressing the gas for each installation, or in some large towns a special high-pressure main is laid from the works or some central point for the supply of gas under such higher pressure where it is required.

The employment of gas under higher pressure for other industrial purposes, especially those in which high temperatures are required, is rapidly extending at the present time, more particularly in towns where gas can be obtained at low rates, and a very considerable increase in the amount employed in this manner appears most probable, especially with a further reduction in the price at which gas is supplied. H. G. C.

GAS, DOWSON. *v.* GAS, WATER.

GAS, GENERATOR. *v.* GAS, WATER.

GAS MANTLES. The discovery, by Goldsworthy Gurney, in 1826, that a piece of dense lime held in the oxy-hydrogen blowpipe flame, gave rise to intense incandescence, may be taken as the starting-point of the utilisation of this phenomenon for the generation of light, as Gurney's discovery was soon afterwards employed in practice by Drummond, who utilised the light whilst making a survey of Ireland; hence it was often known by his name, but is

now more frequently called the oxy-hydrogen or lime light.

The amount of heat necessary to raise a substance to the temperature needed for incandescence depends largely upon the size of the mass to be heated, as the larger it is the more will radiation and conduction tend to prevent the temperature of incandescence being attained, and when, soon after the discovery of the lime light, it was attempted to utilise incandescence for public lighting in Paris, the lime cylinder was replaced by small buttons of zirconia and magnesia, which, being more resistant to atmospheric influences than the lime cylinders, and being far smaller, lasted for a longer period and could more easily be raised to the required temperature.

In this experiment, oxy-coal-gas burners were employed as the heating medium, but the expense soon led to its abandonment. In 1835 Talbot noticed that when a piece of blotting paper was dipped in a solution of a lime salt and was then incinerated in a spirit lamp, the ash which was left, consisting chiefly of lime, was so finely divided that the heat of a spirit-lamp flame was sufficient to raise it to high incandescence.

These early experiments pointed merely to the fact that if a refractory material like lime could be obtained in a sufficiently coherent and finely divided condition, a moderately hot flame would raise it to a temperature at which it would become usefully incandescent.

In 1848 Gillard, in attempting to utilise water gas for lighting as well as heating purposes, made a mantle of fine platinum wire, which, heated to incandescence in the flame, answered its purpose and emitted light for a short period, whilst in 1883 the Fahnehjelm comb (Fig. 1) was introduced for developing light from a flat water-gas flame. It consisted of fine rods of magnesia in a metal setting, which was fixed at the requisite height above a flat-flame burner consuming water gas, and from it a light of about 4½ candles per cub. ft. of gas consumed could be obtained.

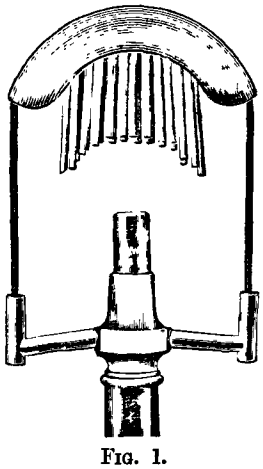


FIG. 1.

Up to the middle of last century, the flame of water gas or of alcohol vapour were the only ones that could have been used to incandesce finely divided refractory material, owing to the deposition of carbon from any luminous flame, but the introduction by Bunsen of the atmospheric burner in the early fifties rendered coal gas available for all heating purposes, and made the mantle a practical possibility.

About 1883 Clamond introduced a form of mantle, consisting of a conical basket of threads of calcined magnesia, which was supported with its apex downwards in a small platinum cage, a flame of coal gas and air being driven down upon it under pressure. It was not, however, until a year later that Dr. Auer von Welsbach, working in Bunsen's laboratory at Heidelberg upon the rare earths, noticed that the oxides of some of the rare metals had a wonderful power of light emissivity when incandescent, and, following up this clue, made the brilliant series of discoveries which gave the world the incandescent mantle.

These discoveries took place in three distinct stages. In his work prior to 1885 he discovered the fact that if a cotton fabric be saturated with a solution of the nitrates of the rare earths, and be then carefully incinerated, an ash is left which is an exact simulacrum of the original fabric, although the burning out of the cellulose reduces it to about one-third of its former size, so that by making a cotton sleeve about three times the size of the Bunsen flame it was intended to fit, saturating it in a solution of the nitrates of the metals of which he required the oxides, and then carefully burning it off over a blowpipe flame, he could obtain a mantle which would fit the outer zone of the Bunsen flame, and, being there heated to incandescence, would emit a useful amount of light.

His first patent, taken out in 1885, covered this part of his invention, and specifies the mixtures of oxides, which he gives as:

60 p.c. of zirconia, or oxide of zirconium.
20 p.c. of oxide of lanthanum.
20 p.c. of oxide of yttrium.

This last oxide may be omitted, and the proportions may be:

50 p.c. of oxide of zirconium.
50 p.c. of oxide of lanthanum.

In place of the oxide of yttrium, ytterite earth may be used, whilst cerite earth containing no didymium and but little cerium may be employed to replace the oxide of lanthanum.

These first mantles were a commercial failure, as they gave a light very little in excess of that yielded by the Clamond basket, and they were so fragile in character that they were unable to withstand the slightest shock.

The amount of light yielded by these mantles varied from 3 to 6 candles per cub. ft. of gas consumed, but it was exceptional to meet with the higher value. Using the purer materials now obtainable, however, mantles made according to the formulæ of the 1885 patent give the following results:—

Composition of mantle	P.c.	Gas consumed cub. ft.	Illuminating power. Total candles	Candles per cub. ft.
I.				
Zirconia	60	5·4	12·9	2·4
Lanthana	20			
Yttria	20			
II.				
Zirconia	50	5·5	9·4	1·7
Lanthana	50			

The lower candle power obtained with mantles made of the purer salts points to the fact that the impurities of the compounds at first employed endowed the older mantles with much of the illuminating power, so that no uniformity in results could be expected, besides which the mixtures of oxides used were continually being varied in hopes of obtaining better results.

In 1886 the second Welsbach patent appeared. This covered the use of thoria either *per se* or mixed with oxides of other rare metals, and it is clear that at this period Welsbach imagined that the oxide of thorium alone had a very high power of light emissivity, but, as a fact, a mantle made of pure thoria emits practically no light, and the amount of light obtainable was due to traces of ceria, which had not been eliminated from the thorium salt in its preparation from thorite and orangite.

Later on, Welsbach discovered this fact, and also found that the addition to thoria of traces of ceria endowed it with the wonderful power of emitting light possessed by the modern mantle, and Mr. Moeller, of the Welsbach Company, took out a patent in England in 1893, in which he protected the use of thoria in combination with very small traces, not exceeding 1 or 2 p.c., of oxides of other rare metals, amongst which was cerium. It was only at this date that the incandescent mantle began to be a commercial success, and in spite of the thousands of experiments which have since been made, no mixture of oxides has been discovered which will give a light comparable with that yielded by the mixture of 99 p.c. thoria with 1 p.c. ceria, which is now universally used in mantle manufacture.

The oxides which can be used in making an incandescent mantle are limited in number, owing to the fact that they must be able to resist atmospheric influences, must be sufficiently refractory to withstand the temperature of the flame for a very long period, and must not be liable to excessive shrinkage during the burning off of the cotton fabric.

The oxides in the following table are those which most nearly fulfil such requirements, and the light given by mantles made from the commercial as well as from the carefully purified salts shows the vast differences that traces of impurity make in their power of emitting light:—

LIGHT EMITTED PER CUBIC FOOT OF GAS BY VARIOUS OXIDES.

		Pure	Commercial
Metallic oxides:			
Zirconia		1·5	3·1
Thoria		0·5	6·0
Earth metals:			
Cerite earths	Ceria	0·4	0·9
	Lanthana	—	6·0
Ytterite earths	Yttria	—	3·2
	Erbia	0·6	1·7
Common earths	Chromium oxide	0·4	0·4
	Alumina	0·6	0·6
Alkaline earth metals:			
Baryta		3·3	3·3
Strontia		5·2	5·5
Magnesia		5·0	5·0

If these oxides be examined for shrinkage, duration, and strength, it is found that only three of them, zirconia, alumina, and thoria, are suitable as the basis of the mantle, and even with these three, zirconia in the hottest part of the flame is liable to considerable and rapid shrinkage, whilst with alumina there is also slow volatilisation, so that the life of the mantle is gradually shortened by the slow wasting away of the threads of the mantle structure. Thoria, however, forms an ideal basis for the mantle, as it is readily shaped at the temperature of the blowpipe flame, is very refractory under the heat of the atmospheric burner for a considerably longer period than any other known oxide, and in the burning off of the cotton fabric there is a minimum of shrinkage.

In the conversion of thorium nitrate into the oxide by heat, the material expands enormously, the final product occupying more than ten times the volume of the original nitrate. This means that the resulting mass is of a spongy character, containing an enormous number of little air cells, which must render it an excellent non-conductor of heat. A mantle made of pure thoria gives practically no light, but if successive small additions of ceria be made to it, the light emitted gradually increases until a ratio of 99 p.c. thoria to 1 of ceria is reached, when the maximum illuminating effect is obtained. The light diminishes with further additions of ceria till, with 10 p.c. of ceria in the mixture, the mantle once more gives practically no illumination. No expansion takes place during the conversion of the cerium nitrate into oxide, the latter occupying about the same amount of space as the original nitrate, hence in the mantle, although the ratio of thoria to ceria is as 99 to 1 by weight, yet by volume it is as 999 to 1.

In the commercial manufacture of mantles, a cotton fabric was first employed knitted in the form of hose, the diameter of which was controlled by the number of needles on the knitting machine, which varied from 50 to 75, the size generally used being knitted by a 65-needle machine, giving to the finished fabric a diameter of 2¼ inches. The resultant hose is cut into suitable lengths, and one end turned over and sewn with thread to form the head of the mantle, (which after impregnation and drying is drawn together with asbestos thread to form the top and a loop for suspension). These lengths were then saturated with the impregnating solution, consisting of a mixture of the thorium and cerium nitrates in the proportion of 99 p.c. of thorium nitrate to 1 p.c. of cerium nitrate, prepared by dissolving 1 kgm. of thorium nitrate and 10 grams of cerium nitrate in 1250 c.c. of water. The mantles then pass through rollers, which are under pressure in order to squeeze out the excess of solution, leaving the fabric retaining the minimum quantity that will give a satisfactory skeleton of oxides after incineration, and this quantity may be taken as 0·7 gram on the rough or 0·5 gram on the finished mantle after trimming. The soaked lengths are next suspended in a drying chamber, the temperature of which is maintained between 80° and 90°F. (27° to 32°C.). In some cases, the head of the mantle is treated with a solution of magnesium and aluminium nitrates, the object being to strengthen this part, which is the most liable to breakage owing to the asbestos thread present in the head. They are again dried, sewn with asbestos thread and 'moulded' by stretching on a wooden mould in order to give them the necessary shape for the next operation, that of 'burning off.' This is done upon suitable blowpipe burners supplied with gas or air under pressure, which gives a flame of a very high temperature, and these are mounted in such a way that either the burner or the mantle can be raised or lowered at the will of the operator, so

that the flame can be made to play on every part, until the whole of the cotton fabric has been destroyed, and the mantle shaped and hardened, leaving a skeleton of oxides formed by the decomposition of the nitrates of the salts

FIG. 2.—COTTON MANTLE BEFORE BURNING OFF.

employed. This skeleton is carefully dipped in a solution of collodion, an average formula for this solution being :

4 p.c. collodion	. 20·0	parts
Ether . .	. 18·3	„
Castor oil .	. 0·96	„
Camphor .	. 1·5	„

the two latter ingredients being added to prevent over-contraction on drying. After dipping, the mantles are hung in a warm room to allow the solvents to evaporate, and they are then trimmed and packed.

As soon as the incandescent mantle became

FIG. 3.—AFTER BURNING OFF.

a success, many attempts were made to evade the Welsbach patents, and the most successful of these consisted in impregnating a solution of nitrocellulose in ether and alcohol with the nitrates of thorium and cerium, and squirting the mixture out through minute orifices in the same way that artificial collodion silk is made. These filaments were then woven into mantle

FIG. 4.—COTTON BEFORE BURNING OFF.

hose, and the collodion basis was denitrated by soaking in an alkaline sulphide, and after washing and drying, the mantle was made from it by the same process as with impregnated cotton. It was found that mantles made in this way were distinctly superior to the cotton mantles, both in life and light emissivity, this being due to the

FIG. 5.—COTTON AFTER BURNING OFF.

difference of the structure of the thoria-ceria residue, which is shown in the photomicrographs, from which it is seen that the cotton (Figs. 2 to 5) gives a closely twisted rope of minute fibres, whilst the collodion (Figs. 6 and 7)

gives a bundle of separate filaments without excessive twist or plait.

The advantages of the collodion mantle were, however, discounted by the cost, which

FIG. 6.—COLLODION BEFORE BURNING OFF.

was much higher than that of the cotton fabric, and attempts were made to find a substitute for cotton which would give the same results as the collodion at a cheaper price, and this was found in ramie fibre, which has now almost entirely replaced cotton for mantle manufacture.

The ramie fibre is produced from a plant of

FIG. 7.—COLLODION AFTER BURNING OFF.

the nettle class, and when freed from its glutinous coating can be woven into a beautiful silk-like material, and when the ramie thread is knitted, impregnated, and made into mantles, the structure is seen to far more nearly approach that of the collodion than of the cotton fabric (Figs. 8 and 9).

Up to 1900, all the mantles used were of the

FIG. 8.—RAMIE BEFORE BURNING OFF.

upright type, supported in the atmospheric burner flame by a central rod of magnesia or an outside iron support from which the mantle was suspended, but owing to the slightly conical shape of the mantle, the maximum light was thrown at an angle a few degrees above the horizontal, whilst the shadow of the fitting was

FIG. 9.—RAMIE AFTER BURNING OFF.

thrown on the surfaces immediately below the burner. In order to overcome this trouble, the idea was introduced by Kent, in 1897, of making an atmospheric burner with a long mixing tube,

the end of which was turned downwards and the flame made to burn in an inverted mantle. It was not, however, until after 1900 that the introduction of the present forms of inverted burner and mantle popularised the idea, which has many advantages in districts where the gas is supplied at a pressure of not less than $\frac{2}{10}$ths, *i.e.* 2 inches of water pressure.

With the inverted mantle, the maximum light is thrown downwards at an angle of 45° below the horizontal, whilst there is no shadow, and the mantle, being fixed to a fire-clay ring which is suspended from lugs on the burner tube, is far less likely to be injured by vibration than is the case with the upright mantle, which needs an antivibrator on the burner if used for street lighting where there is heavy traffic, whilst the slight preheating of the gas and air supply, and the fact that the flame is not hurried away from the mantle as in the case of the upright burner, bring the duty of the mantle up to 25 to 30 candles per cub. ft. of gas consumed.

In making the inverted mantle, the same methods are employed as with the upright, except that the bottom of the fabric is sewn up, after impregnating, squeezing, and drying, with a thread of the same impregnated material, and the top of the hose is bound on to the fire-clay supporting ring with asbestos thread before burning off and shaping.

The burners used with the earliest upright incandescent mantles were small Bunsens of the ordinary type, with a tube about 4 inches in length, fitted with a gallery to carry a chimney and a head stamped out of thin sheet metal. This made a very long fitting which proved an objection in many cases where flat-flame or argand burners had been employed, the result being that the burner tube was shortened, and the head carrying the gallery, which fitted over it, was made so that it but slightly increased the length.

Much ingenuity was expended in devising suitable burners for use with the upright mantle, the chief aim being to ensure a hot steady flame of the right shape with thorough admixture of the air and gas before combustion. Some of these burner heads consisted of open circular slots, others of flat gauze discs with a small baffle in the centre, whilst others were provided with gauze domes and steatite or cut metal tops. All these different varieties, however, suffered from the defect of under-aëration of the gas before combustion, so that a chimney was required in order to create an up-draught and to bring a supply of air from outside the mantle in contact with the burning gas on its surface.

If these burners were used without a chimney, the unburnt gas from the inner zone had to travel a short distance from the surface of the mantle through which it was passing before it obtained the additional air necessary for its complete combustion, with the result that the layer of highest temperature was outside the mantle, which was not in consequence raised to the highest degree of incandescence. When a chimney was used, however, the current of air created by it burnt the gas on the surface of the mantle itself, and the best results were obtained. Burners of this class still form the majority of those employed with upright mantles, and a chimney is a necessity in all burners in which less than one-half the total volume of air needed for the complete combustion of the gas is drawn in, and with a 14- or 15-candle power gas, a 6-inch chimney is generally sufficient to supply the necessary air, whilst with a rich gas a longer chimney is required.

A serious trouble with mantle lighting has been the carbonisation of the mantle, which commences with a slight sooty deposit at one spot, and then rapidly grows over the surface of the mantle, reducing the light emitted and soon destroying the mantle.

When the flame is under-aërated and contains a ratio of less than 2·2 volumes of air to 1 of gas, some methane escapes combustion in the inner zone of the flame, and burns with the carbon monoxide and hydrogen in the outer flame, and it is this which causes the trouble.

On replacing the ordinary tube of a Bunsen burner with one made of platinum, if the ratio of gas and air be so arranged as to give a blue non-luminous flame, on heating the platinum tube the flame becomes luminous, although not to such an extent as would have been obtained from the original gas. If the tube be allowed to cool down, the flame again becomes non-luminous, showing that the luminosity is due to the restoration of heat to the flame and not to any alteration in the composition of the gas. But with a Bunsen burning with a green inner cone, luminosity cannot be produced by heating the mixture of gas and air. On now taking an ordinary Bunsen with a brass tube, and surrounding the blue non-luminous flame with a platinum gauze cylinder so arranged that the sides of the flame heat it to a high temperature, the top of the flame will become luminous, owing to the platinum superheating the flame gases from the inner cone and causing them to decompose with separation of particles of carbon. The same result is obtained with an ordinary mantle open at the top, and it is to this cause that the deposition of carbon on the mantle is due.

Mantle burners in which regeneration has been attempted have also been tried, but the fact that the air or gas can be heated separately and then utilised to give a very hot flame, does not apply to the mixture of the two to any greater extent than is found in the inverted burner, as, when a mixture of air and gas is heated, oxidation of the gas commences, and the loss of combustible matter due to this cause outweighs the advantages of preheating.

Real improvements in the burners employed for mantle heating started in the early nineties, when Chemin and Bandsept began working at the idea of adding air to the gas in small portions so as to gain a more intimate mixture of the two before combustion, and it was the perfecting of this idea in the Kern burner which gave the best chimneyless burner in use.

In this burner, the gas issues from the usual injector into a suction tube, consisting of two cones united at their summits, which increases the proportion of air drawn in with the gas, and the mixture then passes into an enlarged head, where baffling devices ensure thorough mixing, and the burner top is so constructed that the flame of the burning gas is thrown against the mantle, yielding a higher duty than with an ordinary burner and chimney.

The visible duty obtained from the incandescent mantle depends largely upon the pressure at which the gas is supplied, and now that its use has become universal, no gas undertaking should, in their own interest, supply gas to consumers at less than 2 inches ($\frac{29}{10}$) pressure, and when centres of high illuminating value are needed to compete with arc lighting for outside work and large buildings, the light which can be obtained from a mantle can be enormously increased by the use of high-pressure lighting, such as the Keith, Sugg, Selas, and other systems, in which either the gas or air is placed under greater pressure than the ordinary, so that by using what are practically blowpipes, a much larger volume of gas is consumed in a given space, and from 30 to 40 candles light obtained per cubic foot of gas consumed.

The quality of the gas has a certain influence on the light given by the mantle, but not as much as is generally supposed. If an ordinary burner and mantle be tested first with 16-candle gas, then with 15, and finally with 14-candle power gas, it is often found that it gives a better light with the 15 than the 16, and a further improvement with the 14-candle gas. This, however, is dependent upon the fact that the burner is drawing in less than the necessary amount of air to give the best conditions of combustion in the inner zone, and that the right degree of aëration is being more and more nearly approached with the poorer gas. When care is taken to ensure the correct ratio of air and gas consumed in each case, it is found that for qualities of gas between 14 and 18 candle power, there is a gain of about 3 p.c. in the light emitted by the mantle for each candle-illuminating power in the gas.

Seldom in the industrial history of the world has any one invention wrought such alterations in a great manufacture as has been the case with the incandescent mantle, which, being perfected just at the time when electricity was threatening the supremacy of gas as an illuminant, entirely revolutionised the gas industry.

Before the introduction of the mantle, the usual quality of the gas supplied was what was known as 16-candle power, and the light obtained from it by the consumer was anything from 7 to 8 candles per cub. ft. with regenerative burners, down to less than 1 candle per cub. ft. with small flat-flame burners, whilst with the incandescent mantle from 14 to 35 candles per cub. ft. can be obtained.

LIGHT EMITTED PER CUBIC FOOT OF 16-CANDLE GAS CONSUMED PER HOUR.

Burners	Candle units
Incandescent (high pressure)	30 to 35
„ (Kern) . .	20 „ 25
„ (ordinary)	14 „ 19
Regenerative . . .	7 „ 10
Standard argand . .	3·20
Ordinary argand . .	2·90
Union jet flat flame, No. 7 .	2·44
„ „ „ 6 .	2·15
„ „ „ 5 .	1·87
„ „ „ 4 .	1·74
„ „ „ 3 .	1·63
„ „ „ 2 .	1·22
„ „ „ 1 .	0·85
„ „ „ 0 .	0·59

It was also soon found that, in practice, a much poorer gas gave as good or better results with most incandescent mantle burners, and with the general adoption of the mantle, the candle power of the gas supply has been lowered in nearly every large town in England.

At the present time (1912), the annual mantle consumption of the world approximates to:

England . .	38,000,000 mantles
America . .	60,000,000 „
Germany . .	100,000,000 „
France . . .	16,000,000 „
Italy . . .	3,000,000 „
Belgium . .	3,500,000 „
Russia . . .	1,500,000 „

When Welsbach made the first thoria mantles, thorium salts were obtainable only in very small quantities, and from such minerals as thorite and orangite, but with the demand, new sources of supply were found in many directions, and during the last few years, although the amount of thorium nitrate used has more than doubled, the price has fallen by one half, and there appears no fear of a shortage hampering the mantle industry.

Many theories have been brought forward to explain the wonderful light-giving power of the mixture of 99 p.c. thoria and 1 p.c. ceria, but none of them explains both the two facts, *i.e.* that the maximum light is obtained only in the extreme outer layer of the Bunsen flame, where both air and combustible gases are present, and that it is only with 1 p.c. of ceria in the mixture that it is obtained, a mantle of pure thoria or pure ceria giving practically no light.

The probable explanation is that in the mantle, the thoria, being in a porous condition, is a good non-conductor, and owing to this, to its low specific heat and low power of radiating heat, it can be raised to the temperature of the flame; ceria, on the other hand, has a wonderful power of radiation, as shown by Fèry, and has also a catalytic action upon mixtures of combustible gases and oxygen, but its radiation is so great that it cannot be heated in a Bunsen flame to the temperature necessary to give light.

When ceria is added to thoria, the light emitted by the mantle increases until 1 p.c. by weight, or 0·1 p.c. by volume, is present, because the ceria is so insulated by the excess of thoria that it is not only brought up to the temperature of the flame, but by its catalytic power tends to focus the combustion of the extremely attenuated flame gases upon the widely distributed ceria particles, and so raises them to a far higher temperature than the mantle, a temperature, however, which cannot be detected by the thermo-couple, which gives only the average temperature of the mass with which it is in contact, and fails to show the temperature of the 0·1 p.c. of ceria. Addition of more ceria to the mixture causes such a rapid cooling of both mantle and flame by radiation, that the light at once begins to fall; and by the time 10 p.c. of ceria is in the mixture, the mantle gives no more light than a thoria mantle, but a much increased heat radiation.

The work of Le Chatelier, Nernst, Schmidt, and others, shows that the thoria-ceria mixture gives light rays rich in blue, green, and yellow, but poor in red, so that the proportion of energy

radiated as light at the temperature of the mantle is high. V. B. L.

GAS, OIL. Even before the introduction of coal gas, it had been found that oil could be decomposed at a temperature a little below 1000° with the formation of gas of high illuminating power, and when coal gas had overcome the prejudice existing against it in the early years of its inception, several attempts were made to utilise oil instead of coal for the production of illuminating gas, but with no commercial success, owing to the price of the oil.

As early as 1815 a patent was taken by John Taylor for an apparatus for the decomposition of oils, which is interesting as being of much the same type as those still employed; whilst in 1819 Gordon and Heard took out a patent for compressing oil gas, and it was in the liquid separated during compression of this gas that Faraday discovered and isolated benzene.

After this period, oil gas appears to have been but little used until in 1871, when it began to be employed for the lighting of railway carriages on the Continent in place of oil lamps, and it was from this that the firm of Julius Pintsch built up their system of railway-carriage lighting, which soon spread throughout Europe and to England and America, and at a slightly later date oil gas began to be employed for lighting country houses and small villages where the consumption of coal gas was not sufficiently great to allow the erection of coal-gas works.

It was also largely adopted, in the compressed condition, for the lighting of buoys and for other purposes where the portability of cylinders containing it under compression fitted it for special uses in spite of its cost.

The oils now used for the production of gas are generally the blue or green shale oils, although slightly better results may be obtained from the Russian so-called 'solar distillate,' which is obtained by subjecting the residues of Russian oil, left after the lamp-oil fractions have been driven off, to further distillation.

Such oils begin to decompose with evolution of gas at a little under 500°, and the effect of the temperature of the retort on the products is shown in the following table[1]:—

Oil used	Russian 'distillate oil'			
Specific gravity	0·864			
Flash-point	149°F. = 65°C.			
Temperature of retort	500°	700°	900°	1000°
Cubic feet of gas per gallon	12	60	72	84
Percentage of residuals	59·1	22·7	12·7	11·8
Illuminating power, candles per cub. ft.	54·8	50·7	57·1	42·2
The gas contains, p.c.:				
Unsaturated hydrocarbons	39·13	36·56	36·55	22·04
Saturated hydrocarbons	42·41	49·45	49·45	54·83
Hydrogen	13·58	6·26	11·86	21·54
Acetylene	0·052	0·084	0·38	0·46

DISTILLING POINTS OF THE RESIDUES FROM RUSSIAN 'DISTILLATE OIL,' EXPRESSED IN PERCENTAGES OF ORIGINAL RESIDUE. TEMP. = °C.

Temperature	100°–110°	110°–120°	120°–125°	125°–130°	130°–135°	135°–140°	140°–150°	150°–160°	160°–170°	170°–180°	180°–190°	190°–200°	Sp.gr.	Flash-point
														F.
Original oil	—	—	—	—	—	—	—	—	—	1	1	1·5	0·864	149°
Residue after decomposing at:														
500°	—	—	—	—	—	—	4	3·5	0·5	2·5	3	2	0·866	58°
700°	—	—	9	1	2	1·25	9·5	4	1·5	3·5	3	2	0·908	Below 32°
900°	1·6	5	3·3	3·3	5	3·3	6·6	5	6·6	5	—	—	0·926	Below 32°
1000°	—	—	—	—	—	—	10	1	2·5	2	Nil	1	1·019	40°

On decomposing the oil at 500°, the gas is small in quantity and white in colour, the hydrocarbons being present almost entirely as vapours, a large proportion of which go forward with the gas and condonse in the holder, so that the 59 p.c. of residuals condensed in the receiver do not represent the total condensible hydrocarbons.

After condensation of the vapours, the gas amounts only to 12 cub. ft., and contains the saturated and unsaturated hydrocarbons in nearly equal proportion, whilst on examining the tarry residuals it is found that the flash-point is considerably lower than that of the original oil, and also that 15·5 p.c. distils over below 200°, whilst with the original oil only 3·5 comes over below that temperature.

On decomposing the oil at 700°, the yield of gas is increased to 60 cub. ft. per gallon of oil used, and is of a buff colour. In the gas the unsaturated hydrocarbons are 2·5 less in quantity than in the former case, and there are more saturated hydrocarbons. On examining the residuals, the effect of the increase in temperature is found to be most marked: they have decreased in quantity from 59·1 p.c. to 22·7 p.c. of the original oil decomposed, whilst the flash-point has fallen below the freezing-point, and 36·75 p.c. of the residuals distils below 200°. Nine p.c. of the residuals distil at 123°–125°, whilst 9·5 p.c. distils at a temperature of 140°–150°. At 900° the decomposition of the oil yields a still larger volume of gas, in which the percentage of unsaturated hydrocarbons is the same as before, but there is a large increase in the quantity of saturated hydrocarbons, and a slight increase also in the illuminating value of the gas.

The residuals, at this temperature, fall to 12·7 p.c. of the oil used, and on fractionating them more than 1 p.c. distils at 100°, and 5 p.c. at a little over 110°.

On now raising the temperature to 1000°,

[1] Lewes, J. Soc. Chem. Ind. July 30, 1892.

another increase takes place in the volume of the gas, 84 cub. ft. being obtained per gallon of oil decomposed, and the illuminating power falls from 57 to 42. On analysing the gas, it is found that the percentage of saturated hydrocarbons has slightly increased, whilst the percentage of hydrogen has risen from 11·86 to 21·54: on the other hand, the unsaturated hydrocarbons have fallen from 36·5 to 22 p.c. The gas as it leaves the retort has lost its rich chocolate-brown colour, and has become 'sooty' from separation of carbon, and this, as well as the increase in hydrogen, shows that the temperature has been forced to a point at which some of the hydrocarbons, and mainly the unsaturated hydrocarbons, have been decomposed.

The residuals collected from the gas made at this temperature are of nearly the same volume as those obtained by decomposing the oil at 800°, but differ from them in containing nothing with a lower boiling-point than 140°–150°.

From the results obtained in practical working, 900° has been generally adopted as the best retort temperature to employ, whilst the kind of oil used is generally governed by local conditions. The following table gives the results obtained with various grades of oil:—[1]

Name of oil	'Lustre'	Solar distillate	Shale oil	Shale oil
Sp. gr.	0·826	0·8656	0·8495	0·854
Colour	Water white: bluish flourescence.	Reddish brown: green fluorescence	Reddish brown: greenish fluorescence.	Reddish brown: green fluorescence
Fractional distillation	1st drop 115°	1st drop 110°	1st drop 225°	1st drop 250°
	5 p.c. 140	4 p.c. 170	5 p.c. 248	5 p.c. 275
	10 „ 146	10 „ 238	10 „ 255	10 „ 285
	15 „ 152	15 „ 246	15 „ 260	15 „ 288
	20 „ 172	20 „ 252	20 „ 270	20 „ 295
	25 „ 176	25 „ 255	25 „ 275	25 „ 300
	30 „ 190	30 „ 267	30 „ 280	30 „ 320
	40 „ 205	35 „ 271	35 „ 286	35 „ 335
	45 „ 212	40 „ 276	40 „ 290	40 „ 350
	50 „ 217	50 „ 285	45 „ 294	
	55 „ 224	55 „ 291	50 „ 316	
	60 „ 230	60 „ 320	55 „ 350	
	65 „ 234	65 „ 345	Thermometer rising rapidly	
	70 „ 243	Thermometer rising rapidly		
	75 „ 255			
	80 „ 262			
	85 „ 270			
Best results:				
Gas per gal.	74·5 cub. ft.	82·9 cub. ft.	82·5 cub. ft.	66·6 cub. ft.
Illuminating power	49·6 candles	48·2 candles	41·2 candles	62·9 candles

The form of retort and the general apparatus used vary slightly in the processes introduced by Keith, Patterson, Pintsch, and Pope, but a description of the Pintsch plant will suffice to make clear the general principles upon which they all depend.

The retorts are of iron, D-shaped and 10 inches high by 6 feet in length. They rest upon fire-brick, one above the other (Fig. 1), and are connected vertically in pairs. The lid of the upper retort is provided with a siphon pipe, fitted with a funnel at the end into which oil is allowed to flow from an overhead tank, the rate of flow being capable of adjustment by a micrometer cock. The other end of the siphon is continued inside the retort for about 12 inches, and discharges the oil on to a loose thin sheet-iron tray, about 2½ inches deep, which occupies the whole length of the retort, and which is changed and cleaned about once a week. The oil is heated and vapourised in the first retort, and the vapour passes from the further end of the retort downwards into the lower retort, which, being directly over the furnace, is considerably hotter than the upper, the temperature of the retort being a full cherry-red. Here the vapours are 'cracked' and rendered permanently gaseous, and after passage through this retort, they are led by a descension pipe to the hydraulic main. The retorts in the bench are fitted with a test cock, by which the colour of the gas can be ascertained, as this acts as a guide to the work the retort is doing. The gas should be of a pale straw colour: if darker, it is assumed that the temperature is too high, and either the heat of the furnace is slightly reduced, or a little more oil allowed to flow in. Each pair of 10-inch retorts is capable of making 450 cub. ft. of gas per hour.

The tar from the gas-oil retorts having proved to be of little or no value, from time to time attempts were made to do away with the production of liquid residuals as far as possible in the manufacture of oil gas, so that a deposit of pitch or carbon only should be left in the retort. In 1846 Hilary tried to attain this end by placing condenser tubes above the retort, with a view to returning any liquid that condensed back to the retort, where it would be subjected to further distillation, the ultimate products being gas and carbon only. This idea was improved by W. Young, in his process for the manufacture of oil gas.

In Young's process the oil gas, which is obtained by retorting the oil at a moderate temperature, is washed by the oil which is

[1] E. Llewellyn Price, Proc. Incorp. Instit. Gas Eng. 1892.

flowing into the retort, and in this way all condensible vapours are removed, and only permanent gases allowed to pass forward to the purifier. As the oil which has served for the washing is employed for the manufacture of the gas, any permanent gases that may have been absorbed are driven out from it during the retorting, and consequently are not lost.

The retorts are of cast iron and about 10 feet in length, set so as to slope downwards to the back: mouthpieces and ascension pipes are fitted in the usual way, and each mouthpiece has a small cock for testing the colour of the gas, which should be of a pale straw colour, any deeper tint indicating too high a temperature and undue decomposition of the oil. The inflowing oil is admitted through a small tap about 2 feet up the ascension pipe, and drops through the ascending gas on to a steel plate, which extends about 3 feet into the retort, thus obviating the direct impact of the oil on to the bottom of the retort. The temperature employed is between 800° and 900°. From the ascension pipes, the gas passes to the hydraulic main at the back of the retort bench, then through a horizontal condenser to the scrubber, and finally to the holder. The oil cistern is situated above the scrubber, and the oil can be led through all or any of the sections of the scrubber, after which it passes along the bottom

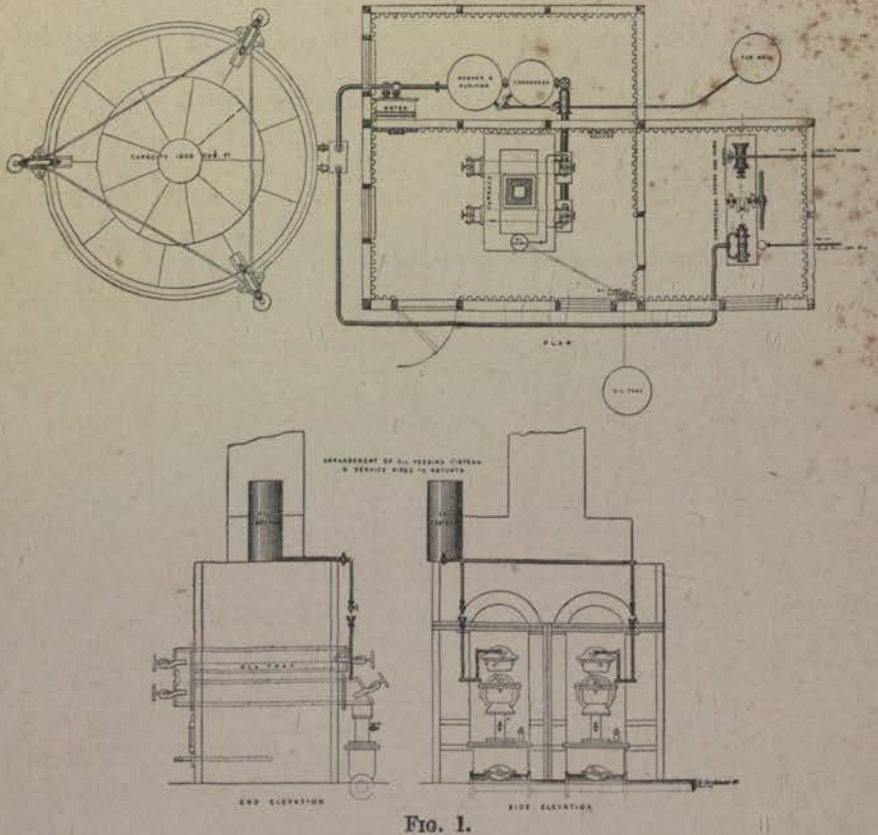


FIG. 1.

of the horizontal condensers to the hydraulic main. From the hydraulic main it enters a small cistern fitted with an indicating float, by which the flow of oil into the retort can be regulated. It will be seen that in this system the oil is always travelling in an opposite direction to the flow of gas.

The oil used is 'blue shale oil' with a specific gravity of about 0·850. Each retort makes 500 cub. ft. of gas per hour, and 5½ cwts. of a very dense graphitic coke is left in the retort for each ton of oil decomposed. When tested on the photometer in burners most suited for its combustion, the gas gives an average of 60 candle power.

The composition of the gases made by the ordinary and by the Young process is shown in the following analyses, the ordinary oil gas being of 50 candle power, and the Young gas 60 candle power:—

	Ordinary	Young
Unsaturated hydrocarbons	33·16	43·83
Saturated hydrocarbons .	45·15	36·30
Hydrogen . . .	19·65	16·85
Carbon dioxide . .	0·50	0·63
Carbon monoxide . .	0·50	0·00
Oxygen	0·60	1·14
Nitrogen . . .	0·44	1·25
	100·00	100·00

In using oil gas for lighting railway carriages and buoys, the gas is forced at six or seven atmospheres pressure into receivers which, in the case of railway carriages, are fixed to the under frame of the carriage. These receivers are connected with a governor, which reduces the pressure of the gas passing through it to 1 or 2 inches of water, at which pressure it is led to the lamps in the carriage roof. The gas is burnt at specially made flat-flame nipples, consuming about a foot of gas per hour, and at this rate yields a light of about 8 candles per burner.

Improvements have been made from time to time by the introduction of horizontal flat flames in place of upright flames, by the use of small regenerative burners, and also by increasing the illuminating value of the oil gas by admixture with acetylene, but the greatest advance that has been made is due to the utilisation of oil gas in the incandescent mantle, which was introduced into this country for railway lighting in 1904. Until the inception of the inverted incandescent mantle, its use for such a purpose as railway lighting was not very successful, as the vibration rapidly destroyed the mantle, and the light, being thrown in an upward direction,

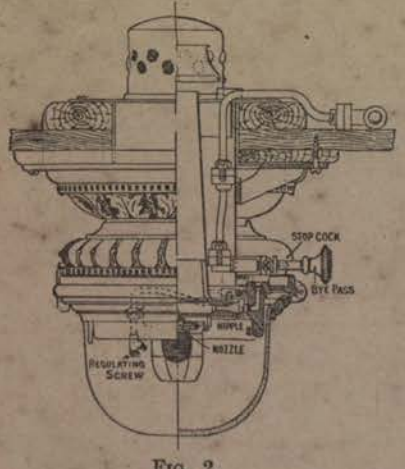
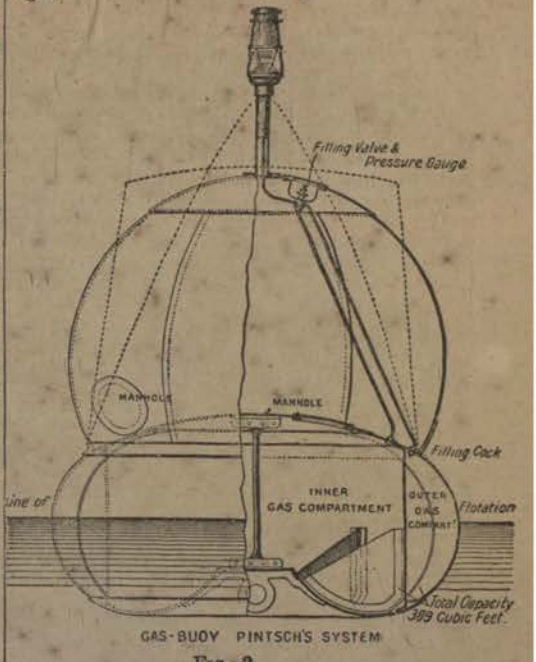


FIG. 2.

necessitated the use of reflectors. With the introduction, however, of the inverted mantle, it was found that the suspension of the mantle on its frame, which merely rested on catches forming part of the nozzle of the burner, acted as a satisfactory anti-vibrator, rendering the mantle far less liable to be affected by shock, whilst in the event of an unusually violent jar breaking it, it is still held in position by a wire cage, which keeps it in contact with the flame, and ensures a light until the mantle can be replaced.

The high calorific value of oil gas, which averages 1000 B.Th.U. per cub. ft., or nearly double that of London coal gas, enables it to be burnt in very small atmospheric burners and mantles, so that a consumption of 0·6 cub. ft. per hour gives 24 candles of illumination, thus trebling the efficiency of the lighting, whilst nearly halving the consumption.

Fig. 2 shows the arrangement of the lantern and burner as used for railway-carriage lighting, whilst Figs. 3 and 4 show the general construction of gas buoys and burners showing a flash light.



GAS-BUOY PINTSCH'S SYSTEM

FIG. 3.

As already mentioned, when oil gas is compressed into the receivers at a pressure of

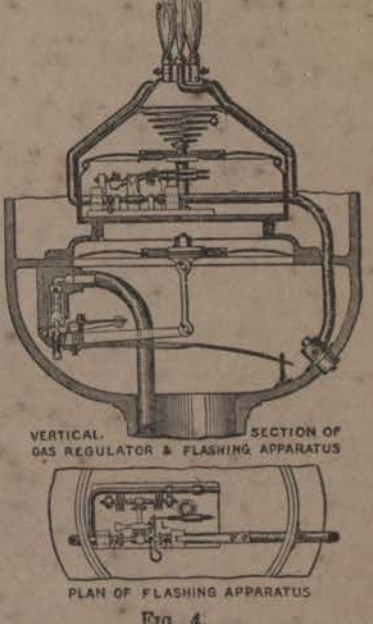


FIG. 4.

about 100 lbs., about a gallon of liquid hydrocarbons separates from 1000 cub. ft. of gas.

occasioning a fall in illuminating power of about 10 candles. This is also observed, but to a smaller extent, in compressing a rich coal gas. This liquid contains as its main constituents, benzene, toluene and hydrocarbons of the ethylene (C_nH_{2n}) group up to normal heptylene, together with some naphthenes and very small quantities of other benzenoid hydrocarbons.

The tar formed during the ordinary process of manufacturing oil gas amounts to about 5 gallons for each 1000 cubic feet of gas. But little use has been found for it. It contains only very small quantities of phenols or basic constituents. In most cases, it is burnt beneath the retorts. One of the chief points in Young's process of making oil gas was that the tar is entirely got rid of, and a very dense and valuable form of carbon obtained instead.

V. B. L.

GAS, PRODUCER, *v.* FUEL and GAS, WATER.

GAS, WATER, is the term applied to the impure gaseous mixture of hydrogen and oxides of carbon formed when steam is passed through incandescent carbon, an action which was probably discovered by Fontana in the 18th century, and was undoubtedly known to Lavoisier.

The first attempt to utilise water gas on a commercial scale dates back to 1824, when Ibbotson sought to increase the volume of gas distilled from his retorts by injecting steam into the red-hot coke remaining at the end of the carbonisation. This idea has been revived on many occasions, but it has always failed, owing to the fact that to make water gas successfully the coke must be kept at a bright red heat, and since the decomposition of the steam absorbs more heat than is given out in the formation of the water gas, the coke charge cooled more rapidly than the heat could be imparted to it through the walls of the retort. When the temperature falls, carbon dioxide is formed in considerable quantities, and had to be withdrawn by lime purification from the mixture of coal gas and water gas before it could be used for illumination in the flat-flame and argand burners then employed. For this reason, such a method of utilising water gas proved too costly in practice. In a modified form, the idea has lately been more successfully revived in the production of low candle-power gas as made in some vertical retort systems.

When steam is passed through a mass of heated carbonaceous material, the composition of the gas formed will vary with the temperature, and to a less extent with other factors, such as the rate of flow and quantity of steam.

It is found by experiment that at temperatures about 600° the reaction is mainly:

$$C+2H_2O=CO_2+2H_2,$$

the quantity of carbon monoxide being small, whilst when 1000° is passed, the reaction more nearly approaches

$$C+H_2O=CO+H_2,$$

the general run of results obtained being:

Temperature of carbon	Percentage composition of resulting gas		
	Hydrogen	Carbon dioxide	Carbon monoxide
600°	66	30	4
700°	65	29	6
800°	62	23	15
900°	54	7	39
1000°	50	2	48

The value of water gas as a fuel largely depends on keeping the percentage of carbon dioxide as low as possible, and it is clear therefore that the temperature of the carbon in whatever form it is used, must be kept at or above 1000°, and that a fall in temperature below 900° causes a large increase in the carbon dioxide.

It is also important, in order to keep down the percentage of carbon dioxide, to avoid any excess of steam over the quantity that can be decomposed by the red-hot carbon, as at temperatures above 900°, some of the carbon monoxide is oxidised by steam to carbon dioxide, according to the equation:

$$CO+H_2O=CO_2+H_2,$$

a reaction which, being reversible, is never completed, but which causes a serious increase in the volume of carbon dioxide in the water gas if an excess of steam be present.

If, however, the temperature in the generator be kept as high as possible, and the volume of steam is properly regulated, water gas is obtained having the average composition:

Hydrogen	51·89
Carbon monoxide	40·08
Carbon dioxide	4·80
Methane	0·10
Nitrogen	3·13
	100·00

together with sulphuretted hydrogen, which varies in quantity with the amount of sulphur in the fuel used.

All the early attempts to make water gas by a continuous process, in which steam was passed through coke in an externally heated retort, proved failures for the reasons given. In 1849 Gillard introduced a process in which he adopted the entirely new idea of raising the temperature of the carbonaceous fuel by blowing air on to it instead of heating it in a retort fired from without: having raised the fuel to incandescence by its own partial combustion, he then shut off the air supply and passed steam through the fuel, until the temperature was so reduced as to necessitate a fresh blowing up by air. It is this principle of 'blow and run' which has since been employed in all the water-gas processes which have had any claims to success.

After Gillard's time, numerous other attempts were made to introduce water gas, but nothing of importance was done until 1875 when Lowe and Tessie du Motay in America inaugurated the present carburetted water-gas systems.

The fact that water gas contains over 90 p.c. of combustible gases, whilst the ordinary producer gas contains only 30 p.c., attracted the attention of some European engineering firms, who required an intense heat for welding purposes, and in the early eighties several plants were installed in Europe for welding

tubular boilers and other work of the same character.

The generator employed consisted of a cupola furnace, about 20 feet in height and 7 feet in diameter, lined with fire-brick, with a constriction a short distance above the hearth, the fire-brick being protected at this point by a water-cooled ring. An air blast is admitted below the water-cooled ring, and in about 10 minutes the ignited fuel is raised to incandescence. The air blast is then cut off, steam is admitted above the top of the fuel, and passing down through it, becomes converted into water gas, which escapes by the same opening as that through which the air blast was admitted, this being opened and closed by means of a water-cooled slide valve of such construction that it is impossible for any explosive mixture of water gas and air to be formed. The water gas passes on to purifiers, which remove sulphuretted hydrogen and carbon dioxide, and the gas is then stored in gas holders. The fuel is fed into the generator at the top, which is closed by a cone: the whole of the steam, air, and water gas pipes being governed by an arrangement of lever valves which renders any explosive mixture impossible. This form of apparatus was installed at the Leeds Forge in 1887.

The impure mixture of hydrogen and carbon monoxide made by such processes burns with a blue non-luminous flame, and is technically known as 'blue water gas,' to distinguish it from the mixture of water gas and oil gas which, introduced in America in 1875, had achieved a great success, and was largely used as a substitute for coal gas under the name of 'carburetted water gas.'

The increase in the price of cannel coal led English gas managers in 1889 to turn their attention to the American practice of mixing carburetted water gas with the coal gas in order to raise its illuminating power. The process was adopted by the Gas Light and Coke Company, and is now used as an auxiliary to coal gas in nearly every large gas works in England.

The reasons that prevented the rapid progress of the 'blue water gas,' except for special purposes, are largely to be found in its poisonous properties and the uneconomic conditions of its manufacture at this period.

It has been shown that in the formation of water gas the perfect decomposition would be represented by the equation:

$$C+H_2O=H_2+CO.$$

A unit weight of hydrogen in burning to water gives out 34,500 calories, and as 2 units burn to form 18 of water, the heat evolved during its production will be $34,500\times2=69,000$ calories: when the 18 units weight of water are again decomposed, this amount of heat will again be absorbed. In this case, however, the water has had to be converted into steam, and so contains an amount of heat equal to the latent heat of steam *plus* the heat used to raise it to the boiling-point. The latent heat of steam is 536 calories per unit weight of water, and to allow for the heat necessary to bring it up to the boiling-point, this is generally called 600. In the present case, we are dealing with 18 units of water as steam, so the heat present in it will be $600\times18=10,800$ calories, and the extra heat used up in decomposing the 18 units weight of water will be $69,000-10,800=58,200$ calories.

The water having been decomposed, its oxygen is available to burn the 12 units of carbon to carbon monoxide, and as in doing this one unit of carbon emits 2489 calories, the 12 will yield $2489\times12=29,868$ calories. If this be deducted from the previous heat deficit, the result is:

$$\begin{array}{r} -58,200 \\ +29,868 \\ \hline -28,332 \end{array}$$

or a shortage of 28,332 for the 12 units of carbon, or 2361 for one. If the units be taken as lbs., 1 lb. of carbon, in decomposing 1·5 lbs. of steam to hydrogen and carbon monoxide, uses up 2361 calories. In order to obtain this amount of heat, 1 lb. of carbon may be burnt to carbon monoxide by an air blast, so obtaining 2489 calories, so that, theoretically, it should be possible to get the required balance of heat by burning half the fuel by an air blast to producer gas, and by a steam jet converting the remaining half to water gas.

In practice, however, the loss of heat taking place from the escape of the hot producer gas, radiation, &c., necessitates the air blast being continued until a far higher proportion of the carbon in the fuel has been consumed, and by this process, instead of 50 p.c. of the carbon of the fuel being converted into water gas, the actual amount is nearer 30 p.c.

In making water gas by such processes as those employed at the Leeds Forge, fuel in the cupola is first raised to incandescence by the combustion of a portion of it under the influence of an air blast, an operation giving as a gaseous product the so-called air-coke gas, of the composition:

Nitrogen	64·5
Carbon monoxide	29·0
Carbon dioxide	4·0
Hydrogen	2·5

Before the temperature of the fuel has been raised to a sufficient point to enable 1000 cub. ft. of water gas to be made by steam injection, no less than 4000 cub. ft. of the air-coke or producer gas have to be formed, and this quantity contains over 44 lbs. of carbon taken from the fuel. The 1000 cub. ft. of water gas are then made, and contain a little over 15 lbs. of carbon, so that the production of the 1000 cub. ft. of water gas means an expenditure in round numbers of 60 lbs. of carbon.

A thousand cubic feet of water gas contain, of combustible constituents:

Hydrogen	2·75 lbs.
Carbon monoxide	30·00 „

and the thermal value will be represented by:

$(2·75\times34,500)+(30\times2,435)=167,925$ calories.

The thermal value of the 60 lbs. of carbon, however, used in making the water gas would be:

$$8137\times60=488,220 \text{ calories.}$$

In other words, the water gas formed has only just about 30 p.c. of the heating value of the carbon from which it has been formed, and this loss of 70 p.c. of the calorific value rendered the use of water gas as made by the old European process impossible, save for special purposes.

When, however, the air coke or producer gas can be at once led away and burnt whilst hot for any purpose, another 223,328 thermal units will be produced, bringing the total calorific value of the two gases up to nearly 80 p.c. of the value of the carbon used in generating them.

If these conditions could have been satisfied, there is no doubt that water gas would long ago have been highly successful, but inasmuch as the producer gas is four times greater in volume than the water gas made, and as the gases are produced intermittently and not continuously, the difficulty of utilising both was almost insurmountable, as, if storage had been provided for the producer gas, the gas holder room required would have been enormous, whilst allowing it to cool down would have rendered it hardly worth burning. In some few installations, a portion of the producer gas has been successfully used in firing boilers and other work of the same character, but the difficulties before enumerated were so great that at the time they practically prohibited the general utilisation of water gas for ordinary fuel purposes.

When the manufacture of carburetted water gas was first successfully carried out by Lowe and Tessie du Motay, it became at once apparent that the producer gas, the loss of which had crippled all water-gas processes, could be utilised in raising chambers filled with chequer brickwork to the high temperature needed to decompose the oils, and so furnish the oil gas which, when mixed with the water gas, rendered the latter luminous. It was, by thus making the carburetted water-gas plant a perfect heat machine, that its greatest success was achieved, as in raising the fuel to incandescence the producer gas, with all its heat in it, was at once burnt with a fresh supply of air in the superheating chambers, the practical loss of heat taking place throughout the whole apparatus being reduced to a minimum.

In all attempts to make water gas prior to 1896, the incandescence of the fuel was always attained by using the air blast with so deep a bed of fuel that the carbon monoxide and residual nitrogen of the air formed the chief gaseous products. It must be remembered that when 1 lb. of carbon combines with oxygen to form carbon monoxide, as when forming producer gas, only 2489 calories are developed, whilst if air be present in sufficient quantity to burn the carbon completely to carbon dioxide, the amount of heat which is evolved is 3·27 times as great, *i.e.* 1 lb. of carbon gives out 8137 calories.

A process was devised by Mr. Carl Dellwik, in which this fact was utilised by adjusting the air supply, and by keeping the level of the incandescent fuel in the generator at a nearly constant height.

Under these conditions, the producer gas ceases to exist as a by-product, and the gases from the blow consist merely of the ordinary non-combustible products of complete combustion, carbon dioxide and nitrogen, the result being that, owing to the high temperature so created in the generator, double the quantity of water gas per lb. of fuel could be made than was before possible, and the extra heat generated minimises the period of blowing, and enables 'runs' or times of steaming to be continued for longer than before.

In the old 'European' process, it was necessary to blow for nearly 10 minutes to bring the fuel bed up to the right temperature, whilst the period during which the incandescence was sufficiently great to decompose the volume of steam used, limited steaming to 4 or 5 minutes, whereas in the Dellwik process, the period of blowing rarely exceeds 2 minutes, and it is possible to steam for from 7 to 10 minutes, according to the condition of the fuel.

The Dellwik generator consists of a sheet-iron shell, lined with fire-brick, which contains the fuel—coke; below the grate level is the valve for the air blast, whilst steam can be admitted either at the top or bottom of the generator. The water gas is provided with two outlets, one at the top and the other at the bottom, connected by a three-way valve. A central stack valve, geared with the air-blast valve, allows the products of the 'blow' to pass away, and through it the fuel is fed into the generator. In practice, the generator is filled to the proper level with coke, which is blown up to vivid incandescence with the air blast, the products passing off through the central stack. When the right temperature is attained, the air is cut off, the central valve being simultaneously closed, and steam is admitted at a carefully regulated rate, which, passing either up or downwards through the coke, is decomposed into water gas. The gas escapes at either of its outlets into a scrubber, where it meets with a stream of water trickling over coke: this cleanses and washes the gas, which is then stored in a holder. When the temperature of the fuel has fallen to a point at which carbon dioxide is formed in excess, the steam is shut off, and the fuel again raised to bright incandescence by the air blast.

Another water gas process in use at several works on the Continent is that known as the 'Kramers and Aarts' process. The novelty in this apparatus consists in having two generators with a regenerating chamber filled with chequer brickwork behind them, so that when the coke in the generators is being raised to incandescence by the air blast, any carbon monoxide that it may contain can be burnt by an extra air supply in the regenerating chamber to heat the chequer work, so that the products escaping up the chimney consist of the products of complete combustion only, and the heat which they contain is further utilised to raise the temperature of the extra air required for the combustion in the generator. When the right temperature of the fuel in the generators has been attained, steam is blown in at the bottom of the first generator, the steam being in excess: the resulting mixture of hydrogen, carbon dioxide, carbon monoxide, and steam is then passed through the regenerator, where it is highly heated, and traverses the second generator, entering at the top and passing downwards through the coke. By this arrangement, the carbon dioxide produced by the excess of steam in the first generator gets reduced to carbon monoxide, whilst any excess of steam is also decomposed into hydrogen. Inasmuch as in this generator the hottest portion of the fuel will be at the bottom, where the air blast has

come more thoroughly in contact with it, the gases finally leave the mass of fuel at the point of highest temperature.

It is well known that when steam is forced in a contrary direction to that in which the air blast has been driven through the generator, the proportion of carbon dioxide is always less than when the steam passes in the same direction as the air blast, and this principle has been used in many forms of generator.

The alterations that have taken place during the last few years in the manufacture of water gas have practically doubled the production of gas per unit weight of fuel used in the generator. The result of several years' practical working at the Leeds Forge with the old 'European' generator, in which during the 'blow' producer gas was formed, gave as an average 34,000 cub. ft. of water gas per ton of coke in the generator, but when this was replaced by the Dellwik generator, it was found that with gas coke of reasonable quality and not containing more than 8 p.c. of ash, the yields rose to over 65,000 cub. ft. per ton, and under special conditions as much as 70,000 cub. ft. could be made.

Gas coke is the fuel most often employed in this country in the generator, and, for effective working, attention should be paid to the size of the coke used. Small sizes can be used only in the smallest generators, and if the coke is too much crushed or contains dust, the dust chokes the air spaces between the pieces of coke and forces the blast and steam to form channels, so lessening the surface of the incandescent fuel exposed to the rapidly flowing gases. At the same time, the coke must not be too large, as that again reduces the surface exposed per cub. ft. of generator space. If it is possible to select the size of coke for any ordinary-sized generator, coke which will not pass through a 3-inch mesh, but will pass through a 5-inch, will give an exposure of about 10 square feet per cub. ft. of generator space, whilst if the size be reduced so that it will not pass through a 1¾ mesh, but will pass through a 2½, the surface of fuel exposed is nearly doubled, and a mixture of these two sizes will, with any ordinary generator, give the best results.

The consumption of steam for the generator and also for the engine driving the blower amounts to about 63 lbs. per 1000 cub. ft. of water gas produced, which will correspond to about 10 lbs. of boiler fuel, and, taking into consideration all charges of production, the cost of water gas per 1000 cub. ft. may be taken at from 3½*d.* to 4*d.*

The economy introduced by the newer methods of making blue water gas has led to a great increase in its consumption for manufacturing purposes on the Continent, and to a more limited extent in this country.

It is found that its use shows a considerable economy in the open-hearth process of steel making, and also in all such operations as welding, annealing, chain making, and other manufactures where an intense but easily regulated temperature is required.

The economies in the modern methods of water-gas production have practically brought into existence the use of welded tubes, which are rapidly superseding rivetted pipes for water-power plant where heavy pressures have to be borne, and the superiority of welded steel pipes in their great resisting power to pressure and shocks and strains of all kinds, the fact that they can be made in almost any length, and their low cost of production, make this comparatively new industry of great importance. A striking example of the utilisation of such pipes is to be seen in the Kinlochleven power installation, consisting of 6 pipe lines, each 1¼ mile in length and 39½ inches in diameter, giving at the works a head of 980 feet of water.

The great advantage of water gas over other gaseous fuels is dependent upon the high thermal value of its combustion as compared with the ordinary producer gases:—

	Cubic feet per lb. at 15°	B.Th.U. per cub. ft.	B.Th.U. per lb.
Water gas	26·6	300	7980
Mond gas	16·4	154	2525
Dowson gas	15·9	148	2353
Suction-plant gas	16·0	135	2160

The poisonous properties of water gas, due to its containing 40 p.c. of carbon monoxide, are a great drawback to its use, as, being odourless, leakages are not readily detected. To overcome this trouble, it has been suggested to admix it with traces of powerfully smelling volatile bodies such as mercaptan.

Dr. J. S. Haldane, who has studied the toxic action of carbon monoxide, gives the following data as to the effect of the gas on man:—

P.c. of carbon monoxide	Effects on man
0·05	After half an hour to 2 hours, giddiness on exertion
0·1	„ „ „ inability to walk.
0·2	„ „ „ loss of consciousness and perhaps final death.
0·4	After half an hour to 2 hours probable death.
1·0	After a few minutes, loss of consciousness, followed before long by death.

The treatment for carbon monoxide poisoning, or 'gassing,' as it is usually termed, is to apply artificial respiration without a moment's delay, if the breathing has ceased or is feeble. The use of oxygen is a valuable adjunct to recovery. Whilst artificial respiration is being applied, the oxygen should be supplied to the patient from a cylinder of compressed oxygen, provided with a length of rubber tubing terminating in a metal mouthpiece which is placed loosely in his mouth, and the oxygen supply should be continued for at least 10 minutes. A person who has been seriously gassed, even if he is not unconscious, should be kept warm and protected as much as possible from cold air, which often causes sudden and dangerous fainting. He should also be prevented from exerting himself by walking, and should be kept lying down for some time. If there is any tendency to spontaneous fainting, a little brandy or whisky should be given.

Many forms of apparatus have been devised for the simultaneous production of water gas and oil gas, the non-luminous water gas being given any desired degree of illuminating value by the admixture with it, whilst hot, of

hydrocarbons obtained by the decomposition of various grades of oil.

At the present time, however, all the successful forms of carburetted water-gas plants are based upon the one originally designed by Lowe in 1875, and the modification most used in this country is that known as the 'Humphrey and Glasgow' carburetted water-gas plant. In this system, the fuel is blown up to incandescence by an air blast in the generator, and the producer gas so formed is burnt in the carburettor and superheater, which are heated up by the combustion to the necessary temperature for decomposing the oil. When the fuel in the generator is sufficiently heated, the air blast is shut off and steam is blown through it, the water gas passing to the top of the carburettor, where it meets the oil, and both are carried down through the carburettor, the oil being thoroughly 'cracked' in its passage. In the superheater, the oil vapours and water gas are subjected to another heating, which has the effect of completely converting the oil vapours into permanent gases. The mixed gases, after being subjected to washing, scrubbing, and condensing, are ready for distribution as carburetted water gas.

The great objection to carburetted water gas in Europe has always been its high percentage of carbon monoxide, viz. from 26 to 30 p.c.

The composition of the mixture will, of course, vary with the proportion of oil gas mixed with the water gas, but the quality most used for enriching coal gas is from 20 to 22 candle gas, and has the approximate composition:

Hydrogen	37·20
Saturated hydrocarbons	18·88
Unsaturated hydrocarbons	12·82
Carbon monoxide	28·26
Carbon dioxide	0·14
Oxygen	0·06
Nitrogen	2·64
	100·00

So that the dilution of water gas by oil gas may be said to reduce the average percentage of carbon monoxide to 28, but, with the exception of a short period in one of the divisions of Liverpool, carburetted water gas alone has never been distributed in this country, although in America about thirty of the largest companies send it out as a domestic supply.

In England, carburetted water gas is used in most large towns as an enricher when this is needed, and also to augment the supply of coal gas, the percentage added to the coal gas varying from 20 to 50 p.c., and experience has shown that as long as the percentage of carbon monoxide in the mixture is below 16, the number of accidents from poisoning due to its use is not appreciably higher than with a pure coal-gas supply. V. B. L.

GASEOUS FUEL *v.* FUEL.

GASES, BLAST FURNACE, *v.* FUEL.

GAULTHERIA OIL *v.* OILS, ESSENTIAL.

GAULTHERIN *v.* GLUCOSIDES.

GEDDA GUM *v.* GUMS.

GELATIN. Gelatin, the purest form of glue (*q.v.*), may be obtained by the action of hot water or of water in presence of dilute acids, on intercellular connective tissue such as the skin, tendons, muscles, &c. Hoofs, bones, intestines, bladders, fishbones, &c., are also made use of for preparing crude gelatin.

According to the process employed by Nelson, the parings, &c., of skins are scored on their surface, and are digested in a dilute soda lye for 10 days. They are then digested at 70°F. in an air-tight, cement-lined vat, and are washed with cold water in a revolving cylinder, and are bleached by means of sulphurous acid gas. After being freed from moisture by pressure, they are digested with water in earthen vessels enclosed in steam chests, and the resultant solution is strained at 100°–120°F. It is then solidified in a thin layer on a marble slab, and is washed free from acid, redissolved at the lowest possible temperature, and dried in thin sheets on nets. According to the process employed by Cox at Gorgie, near Edinburgh, the hides, of which the shoulders and cheeks are preferred, are washed, cut up and pulped by special machinery. The pulp is pressed between rollers, and is mixed with water and heated from 150° to 212°F. A little cow's blood is added to the gelatin solution thus produced, at a temperature not exceeding 170°F., and the solution is further heated, the scum produced by coagulation of the blood albumen being skimmed off. The pure solution remaining is run off and solidified. As prolonged heating impairs the gelatinising power of gelatin, it is preferably dried *in vacuo*.

Several other processes, not differing widely from the above, are also employed. A mixture of vegetable and animal charcoal is sometimes used for purifying dark solutions. Gelatin may also be extracted from bones (which yield one-third of their weight) by causing water to trickle over crushed bones, through which steam is constantly passing (*cf.* GLUE).

Isinglass, the dried swimming bladder of fish, usually contains from 86 to 93 p.c. of gelatin. Russian isinglass is prepared by cutting open and washing the bladder and exposing it to the air with the delicate silvery inner membrane turned upwards. This membrane is stripped off, kneaded in damp cloths and dried. According to Martin, the bladders are first cleansed from blood in hot water, and are cut open and exposed as above, the inner membrane being finally removed by beating and rubbing.

The varieties of isinglass are known by special names dependent on the place of production and their appearance. The Russian varieties are obtained from the sturgeon; Brazilian (sometimes known as Cayenne) from the *Silurus Parkerii*; Manilla and East Indian from an uncertain source. The bladders of cod, hake, and other fish are also employed. *Lump*, *pipe*, and *purse* isinglass are obtained from the unopened bladder, and *leaf* and *honeycomb* from the cut and opened bladder. Long or short *staple* and *book* and *ribbon* isinglass are respectively twisted, folded in packages, and rolled out.

Pure gelatin is an amorphous, brittle, transparent, tasteless, inodorous body, neutral to test paper, and absolutely permanent in dry air. It is heavier than water, and is insoluble in alcohol or ether.

It contains about 50·0 p.c. of carbon, 6·6 p.c. of hydrogen, 18·3 p.c. of nitrogen, and 25·1 p.c. of oxygen. According to Mulder, calcium phosphate

is always present. Schlieper finds sulphur in bone and ivory gelatin to the extent of 0·12–0·14 p.c. Von Bibra has also found it in bone gelatin, and Hammersten (J. Pharm. Chim. 9, 273) has found about 0·7 p.c. of sulphur in fine commercial gelatin.

When moist or in solution, gelatin rapidly putrefies, and possesses the characteristic property of becoming acid at the commencement of the change, although ammonia is finally evolved.

When steeped in water, gelatin takes up from 5 to 10 times its weight of water, a sufficient quantity to dissolve it when warmed to 30°.

A solution containing only 1 p.c. of gelatin becomes a jelly on cooling. Prolonged or repeated heating reduces and finally destroys this property, on which the value of gelatin principally depends, so that the preparation is usually conducted at as low a temperature and as rapidly as possible.

Gelatin is soluble in concentrated acetic acid and in mineral acids, and loses its gelatinising power, but the solution forms a powerful cement for glass, &c. Dumoulin's liquid glue consists of a solution of 2 lbs. glue or gelatin in 1 quart of water and 7 ozs. of nitric acid (1·355 sp.gr.). Gelatin is also soluble in alkalis, and the solution, as well as the acid solution, is lævo-rotatory.

Gelatin is precipitated from solution by tannic acid, forming tannate of gelatin, similar in composition to leather, but not capable of employment as a substitute for that material on account of its want of structure. Corrosive sublimate also precipitates gelatin, but lead acetates and potassium ferrocyanide have not that power.

By prolonged boiling with hydrolytic agents such as sulphuric acid, gelatin yields leucine and glycocoll, but no tyrosine, in which it differs from most other proteids.

The value of gelatin as a food is somewhat doubtful. Gelatin prepared from bones, was largely used by the soldiers and poor of France during the first Revolution, but the idea that its large proportion of nitrogen renders it valuable as a flesh-former appears to be erroneous. It is, however, of limited value as a heat-producer instead of fat and carbohydrates.

Gelatin differs but little in appearance from *chondrin*, which is obtained from cartilaginous tissue, but has a much higher gelatinising power than that substance. Gelatin almost invariably contains chondrin, and, when the proportion of that substance is high, is of considerably less value, especially for the preparation of photographic emulsions, which require a maximum of tenacity.

Chondrin is precipitated from aqueous solution by acetic acid, and is not soluble in excess. Lead acetates, alum, and the sulphates of iron, aluminium, and copper also precipitate chondrin. A rough test for the presence of chondrin in gelatin, useful for photographic work, consists in adding a concentrated solution of chrome alum to a 10 p.c. solution of the gelatin in hot water. If an injurious amount of chondrin be present, the gelatin will set whilst hot. Most photographic gelatins, however, contain but little chondrin.

In judging the value of gelatin, especially for photography, the following properties and tests will be useful: (1) The ash, according to Eder, varies from ½ p.c. in good, to 5 p.c. in inferior, and 10 p.c. in adulterated varieties. According to Abney, however, excellent photographic gelatins sometimes contain as much as 2·5 p.c. (2) A good gelatin will take up from 5 to 10 times its weight of cold water when soaked, *i.e.* sufficient to dissolve it on warming to 30°. (3) The solubilities of gelatins vary considerably. Nelson's No. 1 will dissolve in the ordinary 'cold' water in warm weather, and scarcely sets at 75°F., whereas Coignet's gold label only melts at about 110°F., and sets rapidly. For ordinary photographic emulsions, Abney recommends a mixture of 'hard' and 'soft' gelatins in proportions dependent on the weather, a good mixture containing 1 part of the former to 3 of the latter. (4) The amount of fat in the gelatin should be estimated by precipitating the gelatin by addition of alcohol to the solution. Fatty matters are best removed by skimming the solution or by making a jelly and removing the top. (5) The colour of the solution, the tenacity of a jelly of known strength, and the presence or absence of acid, which is frequently present in sufficient quantity to be distinguished by taste, should also be noted.

Isinglass, although free from chondrin, is not available for photographic purposes on account of its great solubility and inferior tenacity.

Gelatin is largely used for culinary purposes as a vehicle for other materials, and is similarly employed in bacteriology. It is valuable for taking casts and impressions for electrotypy, &c. In photography it is employed, in addition to its use for gelatin dry plates, in the carbon process of photographic printing, which depends on the power of potassium dichromate to render gelatin insoluble when exposed to the action of light. This property is also employed in making an insoluble glue or a waterproofing material, by adding dichromate to glue or gelatin just before use.

It is also used in dyeing, for making inking rollers for printing, and as a size for paper making and painting.

For clearing beer, wine, &c., isinglass is much superior to gelatin. This property is said by some to be due to the fine, net-like structure of the former. Coarse Brazilian isinglass is usually employed. It is 'cut' or dissolved in sulphurous or other acid before use.

GELATIN-DYNAMITE *v.* EXPLOSIVES.

GELIGNITE *v.* EXPLOSIVES.

GELOSE *v.* GUMS.

GELOXITE *v.* EXPLOSIVES.

GELSEMINE *v.* VEGETO-ALKALOIDS.

GEMS, ARTIFICIAL. Almost all the mineral species that find an application in jewellery have been prepared synthetically in the laboratory. These artificial products possess the same chemical composition and physical characters as the natural stones, from which they differ essentially only in their mode of origin. It is therefore necessary to distinguish between artificial (*i.e.* artificially produced) gems and imitation and counterfeit gems: the latter will be treated separately in the next article (GEMS, IMITATION AND COUNTERFEIT).

In nature, these extremely hard and intractable minerals have presumably been formed under conditions of high temperature and pressure during long periods of time. It is

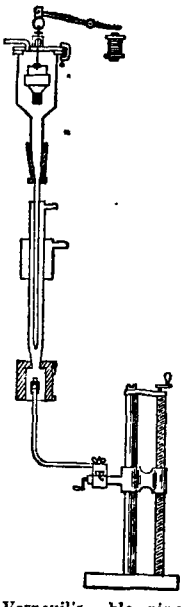
therefore not to be expected that crystals of any appreciable size could be produced in the laboratory. The high intrinsic value of the products has, however, offered an incentive to repeated experiments; and recently the production of corundum of gem-quality and of various colours has been effected with a high degree of commercial success and in a most unexpected manner. Corundum and spinel are the only gem-stones that have, up to the present, been produced artificially of a size and quality suitable for jewellery.

Diamond has been produced artificially by H. Moissan and others (*v.* DIAMOND); but the many attempts made to induce the common element carbon to crystallise in this form have not resulted in the production of crystals larger than 0·4 mm. across. An interesting account of Moissan's extensive researches in this direction is given in his book Le Four Électrique, 1897 (English translation by A. T. de Mouilpied, The Electric Furnace, 1904).

Corundum was produced artificially first by M. A. Gaudin in 1837, and Fremy and Fiel in 1877 succeeded in producing crystals of fair size and of a fine ruby-red colour (E. Fremy, Synthèse du Rubis, 1891; *v.* CORUNDUM). The largest of these crystals weighed ⅛ carat (0·07 gram), and a few were faceted and mounted as gems; but owing to the extreme thinness of the small platy crystals, they were of no commercial value. About the year 1885 rubies of some size appeared mysteriously on the market, it is said from Geneva: whilst some of these were optically isotropic and softer than true ruby, being of the nature of alumina glass, others were crystalline and identical with natural ruby in their characters. These were known as 'reconstructed rubies,' and had probably been produced by fusing together small natural stones.

In 1902 A. Verneuil (Production artificielle du rubis par fusion, Compt. rend. 1902, 135, 791; Ann. Chim. Phys. 1904, [8] 3, 20), who had previously assisted Fremy in his experiments, described a new and eminently successful method for the artificial production of rubies of the finest gem-quality. His apparatus consists of an oxy-hydrogen blowpipe placed vertically, the inner oxygen tube of which is enlarged at its upper end to contain a fine sieve holding the alumina powder used in the process. The periodic tapping on the sieve of a small hammer, actuated by an electro-magnet or a rotating cam, causes a small continuous feed of the alumina powder to fall down the oxygen tube. Beneath the nozzle of the blowpipe is a support terminating in a small rod of fused alumina, the position of which can be adjusted by screw motions. The blowpipe nozzle and the support are enclosed in a box in order to avoid sudden changes in temperature. Hydrogen was used in the early experiments, but in the commercial process coal-gas is used. The flame, with a temperature of 1800°-2000°, must be a reducing one with an excess of hydrogen or carbon. The fine particles of alumina ejected through the nozzle of the blowpipe fall on the alumina support, and, fusing together, build up by accretion a pear-shaped mass, which continues to grow both in height and diameter as the support is gradually lowered.

These pear-shaped masses of manufactured ruby ('rubis scientifique,' 'rubis synthétique') grow at the rate of about 12 carats per hour, and they may attain a weight of 80 carats (about 16 grams). One operator can attend to ten or a dozen machines; and the total output in Paris exceeds five million carats (about 1000 kilos. or 1 ton) per annum. The price of the uncut material is less than 1*s.* per carat. Now, the curious feature of these masses of fused alumina is that each one of them is a single individual crystal, and not, as might have been expected, an aggregate of crystals or simply an alumina glass. Although the sides of the drop are smooth with a glassy aspect, the rounded end (the upper and last-formed portion in the apparatus) is usually roughened with a fine crystalline reticulation. The narrow stem, where the drop is broken off the support, often shows a bright cleavage surface. The optic axis usually coincides with the axis of the pear-shaped mass, and a section cut perpendicular to this exhibits in the polariscope a typical uniaxial interference-figure. The sp.gr. (3·98–4·0), hardness, dichroism, refractive indices, &c., of this artificial corundum are the same as for the natural mineral. The material further possesses the same transparency, clearness, and rich colours as natural crystals of the best gem-quality. The only means of distinguishing between the two is afforded by certain minute irregularities of internal structure. With a hand-lens or under the microscope, the artificial corundum often, though not invariably, shows minute rounded cavities and curved streaks; whilst in the natural stones the cavities are angular and the streaks are straight.



Verneuil's blowpipe for the artificial production of ruby.

When the material supplied to the Verneuil blowpipe consists of pure alumina powder (prepared by precipitation with ammonia from pure ammonium alum), the crystallised product is perfectly colourless and clear ('white sapphire'). In the early experiments, powdered natural ruby was used as the material. The best ruby-red tint is given by the addition of 2½ p.c. of chromic oxide (homogeneously mixed with the alumina by precipitating the two together from a mixed solution of ammonium alum and chromium alum). Smaller proportions of chromic oxide produce a lighter shade of red or pink, and such artificial gems have been erroneously called 'scientific topaz.' The addition of nickel oxide produces a rich yellow colour. Cobalt oxide will not produce a blue colour with alumina alone, but a fine blue is obtained when some magnesia (or lime) is present (L. Paris, Compt. rend. 1908, 147, 933; A. Verneuil, *ibid.* 1059); but now the product,

instead of being corundum, is the cubic and optically isotropic mineral *spinel* ($MgAl_2O_4$). Attempts to produce a blue corundum (*i.e.* sapphire) have repeatedly failed until quite recently, when it was obtained by A. Verneuil (Compt. rend. 1910, 150, 185) by the addition of titanic oxide (TiO_2, 0·5 p.c.) and magnetic oxide of iron (Fe_3O_4, 1·5 p.c.). Analysis of this artificial sapphire gave: Al_2O_3, 99·83–99·85 p.c.; TiO_2, 0·11–0·13 p.c.; Fe_2O_3, trace; sp.gr. 3·977–4·01 (A. J. Moses, Amer. J. Sci. 1910, 30, 271). A peculiar stone which has been sold as 'synthetical alexandrite,' exhibits, like the true alexandrite (a variety of chrysoberyl, $BeAl_2O_4$), a green colour by daylight and a red colour by lamp-light: this is in reality artificial corundum, and the change in colour may be attributed to the presence of colloidal chromic oxide (as suggested in the case of alexandrite by O. Hauser, Zeitsch. angew. Chem. 1910, 23, 1464).

References.—In addition to the papers by Verneuil and others quoted above, *see* J. Boyer, La synthèse des pierres précieuses, Paris, 1909; R. Brauns, Über künstliche Edelsteine, Aus der Natur. Jahrg. 1908–9, 647; 1909, 51.

On the artificial production of minerals in general, *see* L. Bourgeois, Reproduction artificielle des minéraux, Paris, 1884 (Encycl. chim. de Fremy); P. Tschirwinsky, Reproduction artificielle de minéraux au XIXe. siècle, Kieff, 1903–1906. L. J. S.

GEMS, IMITATION AND COUNTERFEIT. As pointed out in the preceding article, it is necessary to distinguish between artificial (*i.e.* artificially produced) gems and imitation and counterfeit gems. Owing to their rarity and high value, gem-stones have been imitated in various kinds of material since very early times. For instance, although a few of the ancient Egyptian scarabs were cut in genuine turquoise, the great majority of them were made of a blue pottery or faience; and amongst the Romans, coloured glass was used for the imitation of the various transparent coloured gem-stones.

The material most extensively used for the manufacture of imitation gems is a heavy lead (flint) glass known as *paste* or *strass*. This is prepared by fusing in a crucible a mixture of powdered rock-crystal (38–59 p.c.), red lead (Pb_3O_4, 28–53 p.c.), potassium carbonate (K_2CO_3, 8–14 p.c.), together with a small proportion of borax, white arsenic, or saltpetre. Different recipes vary widely, the amount of lead present depending on the refractive index of the gem to be imitated. A dense flint-glass of sp.gr. 3·54 (*i.e.* about the same as diamond) has $n_D=1·6118$ and dispersion $n_{G'}-n_{A'}=0·0315$; and an extra-dense flint-glass of sp.gr. 5·004 has $n_D=1·7784$ and dispersion $n_{G'}-n_{A'}=0·0568$ (the corresponding values for diamond being 2·4173 and 0·0574 respectively). Optical values still higher are obtained by replacing the potassium by thallium: the sp.gr. of a thallium-lead glass may be as high as 5·6. To obtain the best results in the manufacture of strass, the materials employed must be quite pure; and the fusion carefully conducted, in order to avoid bubbles and streaks. Imitation diamonds (so-called 'Parisian diamonds,' &c.) are cut from the colourless paste. To prepare coloured pastes the colourless paste is powdered, intimately mixed with various metallic oxides or other substances, and again fused. A blue colour is obtained with cobalt oxide; green, with cupric oxide or chromic oxide; red, with cuprous oxide, gold chloride, or purple of Cassius; yellow, with silver chloride, antimony oxide or red antimony, or (in leadless glasses) with coal and a little manganese oxide; black, with tin oxide, manganese oxide, and hammer-slag. An opaque white glass, or enamel, is obtained by the addition of tin oxide, calcium phosphate, or bone-ashes; this may be suitably coloured to imitate opaque stones (*e.g.* turquoise) by the addition of metallic oxides.

These glasses often afford very clever imitations of the various precious stones, resembling them so closely, indeed, that without examination they may be readily mistaken for the genuine article. They are, however, all remarkable for their low degree of hardness, less than that of ordinary window-glass, and they can be readily scratched with a knife. In course of time, they display a dark leaden tarnish on their surface, and when worn in jewellery their edges become rubbed and chipped. When examined with a magnifying-lens, bubbles and streaks are often to be seen in them. Optically they are isotropic and lacking in dichroism.

To avoid the effects of abrasion in wear, and also no doubt as a deception in case the test of hardness is applied, these soft materials are sometimes faced with a harder material such as rock-crystal or colourless topaz. In the *doublet*, the upper portion, above the girdle, consists of this harder, colourless material, while the lower portion, protected in the setting, consists of coloured strass which imparts its fine colour and brilliancy to the whole. The *triplet* consists of an upper and a lower portion of harder material, with a layer of the coloured strass between. Such counterfeits can, of course, be readily detected when the unmounted gem is viewed sideways, but when it is mounted in its setting detection is not so easy. Doublets and triplets are also built up of genuine stones, with the object of improving the colour, and of producing a gem of larger size.

Another kind of fraud sometimes practised with precious stones is the substitution of less valuable stones for more valuable. Unfortunately, the nomenclature of gems, as adopted by jewellers, rather offers an opening in this direction. Thus stones of a red colour are often known collectively as ruby with some qualifying prefix: *e.g.* 'spinel-ruby' (=spinel), 'Cape ruby' (=pyrope garnet), and 'Siberian ruby' (=tourmaline), the true ruby ('Oriental ruby' of jewellers) being, of course, corundum; or again, 'Oriental emerald' (=corundum), 'Uralian emerald' (=demantoid garnet), 'lithia-emerald' (=spodumene) and 'Brazilian emerald' (=tourmaline), the true emerald being beryl of a grass-green colour. In the same way, yellow quartz ('Spanish topaz' or 'Occidental topaz') is often mistaken for and sold as topaz. Other deceptive terms of a like nature are 'Marmorosch diamonds,' 'Cornish diamonds,' 'Bristol diamonds,' &c., for small sparkling crystals of quartz; and 'Matura diamonds' (from Matura in Ceylon) for zircon of a brilliant

lustre, which has been decolourised by the application of heat. The latter, as well as colourless corundum ('white sapphire'), have occasionally been passed off as diamonds.

Other attempts have been made to produce gems of much the same chemical composition as the genuine stones. For example, green glass with the composition of emerald. Very successful imitations of turquoise have been obtained by submitting to pressure a precipitate having the same composition as the natural mineral.

The artificial colouring of natural stones is also extensively practised. Almost all cut agates have been so treated (*v.* AGATE). Chalcedony can be so cleverly coloured a delicate green with salts of nickel or chromium, as to be practically indistinguishable from the more expensive chrysoprase. The colour of many gem-stones can be changed by heating or by exposure to the emanations of radium. A trick of the meanest kind is to smear violet ink or other bluish colouring matter on the surface of a yellowish ('off-coloured') diamond, so giving it the appearance of a colourless gem.

Reference.—M. Bauer, Precious Stones, English transl. by L. J. Spencer, 1904.

L. J. S.

GENISTA TINCTORIA *v.* DYER'S BROOM.

GENISTEIN *v.* DYER'S BROOM.

GENTIAN. *Gentianæ radix.* (*Racine de Gentiane*, Fr.; *Enzianwurzel*, Ger.) The dried root of the *Gentiana lutea* (Linn.) (Bentl. a. Trim. 182) is used in medicine as a bitter tonic. Its physiological activity appears to depend upon the presence of a small proportion of a bitter crystalline glucoside, *gentiopicrin*, *gentianbitter*, or *gentianin*, which was first obtained in a definite form by Kromayer (Die Bitterstoffe, Erlangen, 1861, 105: Gm. 16, 193).

To prepare gentiopicrin, the fresh gentian root is cut into small pieces and quickly dropped into boiling alcohol in order to destroy the ferment which is present in the root and would otherwise lead to loss of glucoside. The liquid is boiled for 30 minutes, cooled, and filtered. The alcohol is then removed by evaporation, the residual liquid mixed with calcium carbonate, filtered, evaporated to a syrup, and allowed to stand for a fortnight to crystallise. The crystals obtained are purified by recrystallisation from a mixture of equal volumes of chloroform and 95 p.c. alcohol (Bourquelot and Hérissey, Compt. rend. 131, 113). Gentiopicrin has the composition $C_{16}H_{20}O_9.\frac{1}{2}H_2O$. It melts at 122°, or, when anhydrous, at 191° (Tanret, *ibid.* 141, 207). By the action of dilute acids or emulsin, gentiopicrin breaks up into dextrose, and flakes of a yellow amorphous compound *gentiogenin*, which is soluble in alcohol, but almost insoluble in water.

The mother liquors resulting from the purification of gentiopicrin contain a compound, *gentiin* $C_{25}H_{24}O_{14}$, which forms microscopic slightly yellow needles, m.p. 274° (decomp.). It is slowly hydrolysed by dilute sulphuric acid at 100°, forming dextrose (1 mol.), xylose (1 mol.), and *gentienin* $C_{14}H_{10}O_5$ (1 mol.). The last-named compound, on heating, begins to sublime at 195° and melts at 225°. It is isomeric with gentisin, another constituent of gentian to be described presently, but melts at a lower temperature, and gives a yellow colouration with nitric acid. Gentisin, under these circumstances, gives a green colour (Tanret, Compt. rend. 141, 263). The alcoholic extract of gentian root, from which gentiopicrin separates, also contains an amorphous glucoside, *gentiomarin*, which has the composition $C_{16}H_{22}O_{10}$ or $C_{16}H_{20}O_{10}$. On hydrolysis with acids, gentiomarin yields an amorphous brown substance; with emulsin, dextrose and an amorphous maroon-coloured substance distinct from gentiogenin (Tanret, Bull. Soc. chim. [iii.] 33, 1071).

Gentian also contains, in very small proportion, another compound which, though physiologically inactive, is much better known. It is a yellow crystalline acid, *gentianic acid*, *gentisin*, or *gentianin* $C_{14}H_{10}O_5$, and by the earlier investigators (Gm. 16, 178) was confused with gentian-bitter or gentiopicrin, and to both these compounds the name 'gentianin' has been applied. To obtain gentianic acid, the powdered root, after removal of pectin and saccharine constituents, by prolonged maceration in cold water, is extracted with boiling alcohol. Most of the alcohol is removed from the solution by distillation, when on the addition of water a precipitate forms consisting of impure gentianic acid. This, after washing with ether, may be purified further by recrystallisation from alcohol or by conversion into a potassium salt, and regeneration with acetic acid (Henry and Caventou, J. Pharm. Chim. 7, 173; Trommsdorff, Annalen, 21, 134; Leconte, *ibid.* 25, 202; Baumert, *ibid.* 62, 106; Hlasiwetz and Habermann, *ibid.* 175, 63; 180, 348).

Gentisin crystallises in large pale-yellow silky needles. Heated to 200°, it darkens in colour, and sublimes with decomposition at 300°–400°. It is nearly insoluble in water, at 16°, 1 part requiring 3630 parts of water for solution, but in alkaline solutions and in hot alcohol it dissolves readily. Melted with potash, acetic acid, phloroglucin and gentisic acid

$$C_6H_3(COOH)(OH)(OH)$$

(1 : 2 : 5) are formed (H. and H.).

Gentisin has been obtained synthetically by Kostanecki and Tambor (Monatsh. 15, 1), and is the methyl ether of gentisein, 1 : 3 : 7-trihydroxyxanthone $OH\cdot C_6H_3\langle{}^{O}_{CO}\rangle C_6H_2(OH)_2$ which compound is formed when the methyl group is eliminated from gentisin by boiling with hydriodic acid (Kostanecki, Monatsh. 12, 205).

Pectin is present in gentian root in large proportion. This yields mucic acid on oxidation by dilute nitric acid and arabinose on hydrolysis with dilute sulphuric acid (Bourquelot and Hérissey, J. Pharm. Chim. [vi.] 8, 49). Fermentable sugar is present in so large a proportion that it has led to the root being employed in Switzerland and Bavaria in the manufacture of spirit. Investigations carried out by Bourquelot and his co-workers (Bourquelot and Nardin, Compt. rend. 126, 280; Bourquelot and Hérissey, *ibid.* 131, 750; 135, 290) show that fresh gentian root contains *gentianose*, a hexotriose, $C_{18}H_{32}O_{16}$, which melts at 207°–209°, and is dextro-rotatory. It does not reduce Fehling's solution, but, if boiled with dilute sulphuric acid or acted upon by invertase, it becomes lævo-rotatory, and acquires considerable

reducing power, having become hydrolysed into lævulose and a new hexobiose, *gentiobiose*, which, by more vigorous treatment, can be hydrolysed into 2 molecules of dextrose.

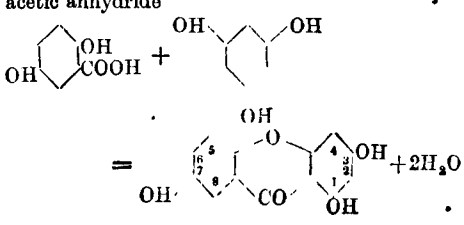
For the detection of gentian-bitter in beer, *v.* Dragendorff (Chem. Zentr. 1881, 285 and 299); Allen (Analyst, 12, 107; 13, 43). A. S.

GENTIAN ROOT. The *Gentiana lutea* (Linn.), from which the gentian root is derived, chiefly occurs in mountainous districts, especially in Switzerland and the Tyrol. There is present in the root of this and other species of *gentiana* a bitter principle which is said to possess valuable tonic virtues, and on this account some quantity of the material is imported into this country for medicinal purposes.

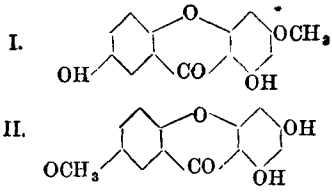
Gentisin, the colouring matter of gentian root, was first isolated by Henry and Caventou (J. Pharm. Chim. 1821, 178), and was shown by Baumert (Annalen, 62, 106) to possess the formula $C_{14}H_{10}O_5$. Hlasiwetz and Habermann (*ibid.* 175, 63; 180, 343), somewhat later, found that gentisin contains two hydroxyl groups, and that, when fused with potassium hydrate, *phlorglucinol* and *gentisic acid* (hydroquinone carboxylic acid) are produced from it. By the action of hydrochloric acid on fused gentisin, methyl chloride was evolved, a probable indication of the presence of a methoxy- group. To prepare gentisin (Baumert, *l.c.*), the root is well washed with water, then extracted with alcohol, and the extract evaporated to a small bulk. The residue is washed with water to remove the bitter principle, and then with ether to extract plant wax. For purification, the crude colouring matter is repeatedly crystallised from alcohol: 10 kilos. of the root yield about 4 grams of the substance. Gentisin crystallises in yellow needles, is sparingly soluble in alcohol, and dissolved in alkaline solutions with a yellow colour.

Gentisein $C_{13}H_8O_5,2H_2O$. When gentisin is digested with boiling hydriodic acid, it is converted into gentisein with evolution of 1 molecule of methyl iodide. Gentisein consists of straw-yellow needles, melting at 315°, and gives with sodium amalgam a blood-red colouration, whereas gentisin, by a similar method, yields a deep green-coloured liquid (Kostanecki, Monatsh. 12, 205). By the action of acetic anhydride, gentisein is converted into a *triacetyl* derivative, $C_{13}H_5O_5(C_2H_3O)_3$, needles, m.p. 226° (Kostanecki, *l.c.*); but on methylation with methyl iodide, a *dimethyl ether* $C_{13}H_7O_2(OH)(OCH_3)_2$, yellow needles, m.p. 167°, is produced (Kostanecki and Schmidt, Monatsh. 12, 318).

Partial methylation converts gentisein into gentisin, and it is thus certain that the latter consists of *gentisein monomethyl ether*. Kostanecki and Tambor (Monatsh. 15, 1) obtained gentisein by distilling a mixture of phloroglucinol and hydroquinone carboxylic acid with acetic anhydride



and its constitution is therefore represented as 1:3:7-trihydroxy-xanthone. By a study of *disazobenzene-gentisin*, $C_{14}H_8O_5(C_6H_5N_2)_2$, scarlet-red needles, m.p. 251°–252° (Perkin, Chem. Soc. Trans. 73, 1028), which gives the diacetyl derivative, $C_{14}H_6O_5(C_2H_3O)_2(C_6H_5N_2)_2$, orange-red needles, m.p. 218°–220°, it has been shown that gentisin itself possesses the constitution I.



As gentisin yields by means of methyl iodide only a monomethyl ether, the original methoxy-group cannot be in the position (1). On the other hand, if gentisin is represented by the formula II., the azobenzene groups would enter the positions 4 and 2, and from such a compound an acetyl-derivative cannot be obtained (compare *disazobenzene phloroglucinol*).

Gentisin is a feeble dyestuff, and gives on wool mordanted with chromium, aluminium, and tin respectively, pale-green yellow, pale bright yellow, and very pale cream-coloured shades (Perkin and Hummel, Chem. Soc. Trans. 1896, 69, 1290). A. G. P.

GENTIAN-BITTER *v.* GENTIAN.

GENTIAN BLUE 6 B. *Spirit Soluble Blue, Spirit Blue O, Opal Blue v.* TRIPHENYLMETHANE COLOURING MATTERS.

GENTIANIC ACID, GENTIANIN *v.* GENTIAN.

GENTIANOSE *v.* CARBOHYDRATES.

GENTIIN *v.* GLUCOSIDES.

GENTIOGENIN *v.* GENTIAN.

GENTIOPICRIN *v.* GENTIAN; *also* GLUCOSIDES.

GENTISIC ACID *v.* GENTIAN and PROTOCATECHUIC ACID.

GENTISIN *v.* GENTIAN ROOT and GENTIAN.

GEOSOTE *v.* SYNTHETIC DRUGS.

GERANINE *v.* AZO- COLOURING MATTERS and PRIMULINE.

GERANIUM OIL *v.* OILS, ESSENTIAL.

GERMANIUM, Ge. At. wt. 72·5 (Winkler), is the *ekasilicon* predicted by Mendeléeff. It was discovered by Winkler in 1866 in *argyrodite* $GeS_2,4Ag_2S$, in which it is present to the extent of about 6–7 p.c. (Kolbeck, Centr. Min. 1908, 331). It is also present in *canfieldite*, *franckeite*, and *brongniardite* (Prior and Spencer, Min. Mag. 1898, 12, 5; Shroutschoff, J. Russ. Phys. Chem. Soc. 1892, 130), but its presence in *euxenite* and *samarskite* has been denied by Lincio (Centr. Min. 1904, 142). The metal is obtained by the reduction of the dioxide with carbon at a red heat. It is a greyish-white, brittle, readily powdered lustrous metal of sp.gr. 5·469, which melts at 500°, and does not volatilise at 1350°. It oxidises in air at high temperatures, combines directly with the halogens, is insoluble in hydrochloric acid, and dissolves in *aqua regia*, forming the dioxide.

Compounds.—The metal is tetravalent, and its compounds resemble those of the silicon group.

Germanium dioxide GeO_2 is obtained from argyrodite by treating the latter with nitre and

potassium carbonate at a red heat, then with acid, after which it is purified by being converted into the sulphide, which is roasted and treated with nitric acid. The oxide forms a white powder having acid properties, but soluble in acids, and is readily reduced by carbon, sodium or magnesium. A colloidal solution of germanium hydroxide is obtained by decomposing an alkaline solution of the dioxide with carbon dioxide.

Germanous oxide GeO is a greyish-black powder, and the corresponding hydroxide $Ge(OH)_2$ is a yellow powder obtained by the action of alkalis on germanium chloroform or chloride. According to Hantzsch (Zeitsch. anorg. Chem. 1902, 30, 289), in aqueous solution it is a weak monobasic acid, and has the constitution HGeO·OH, being analogous to formic acid.

Germanium chloroform $GeHCl_3$ is obtained when germanium is heated in a current of hydrogen chloride, a colourless liquid being thus formed, which separates into two layers, of which the heavier is germanium chloroform; it is a colourless fuming liquid, b.p. 75°. The lighter liquid is *germanium oxychloride*, $GeOCl_2$; it is similar in properties to the chloroform, but is less mobile, and boils above 100°. *Germanium dichloride* $GeCl_2$, the *tetrachloride* $GeCl_4$, and the corresponding tetrabromide, -iodide, and -ethide $GeEt_4$, are also known.

Germanium tetrafluoride $GeF_4,3H_2O$ combines with hydrofluoric acid, forming *germanofluoric acid*, of which the *potassium* salt K_2GeF_6 forms hexagonal crystals isomorphous with those of ammonium silicofluoride.

Germanium disulphide GeS_2 is the most characteristic of the germanium derivatives, and is prepared by passing sulphuretted hydrogen in a solution of germanium dioxide; it is a white powder, soluble in water to some extent and in ammonium sulphide (Vogelen, Zeitsch. anorg. Chem. 1902, 30, 329). The monosulphide GeS and *thio*germanates are also known (J. pr. Chem. 1887, [2] 36, 177; Ber. 1888, 21, 131).

Germanium hydride GeH_4 is formed when germanium chloride is reduced with sodium amalgam. It is also formed as a mirror in the Marsh apparatus, as in the arsenic test. The mirror is red by transmitted and green by reflected light, is soluble in sodium hypochlorite, but with difficulty in hot hydrochloric acid. With sulphuretted hydrogen it forms the sulphide; heated in air it gives the dioxide, whilst with silver nitrate it forms a black silver germanium compound, probably $GeAg_4$ (Vogelen, *l.c.* 325).

GERMOL. A disinfectant consisting of crude cresols.

GESILIT *v.* EXPLOSIVES.

GETAH WAX *v.* WAXES.

GHATTI *v.* GUMS.

GHEE. A clarified butter used in the East mainly for cooking.

GIALLOLINO or **NAPLES YELLOW** *v.* PIGMENTS.

GIANT POWDER *v.* EXPLOSIVES.

GILO, GOLANCHA, and **GULOH.** Indian names for *Tinospora cordifolia* (Miers). This plant flourishes in India, the drug being sold extensively in the bazaars as a tonic and antiperiodic, in the form of cylindrical pieces, 2 to 5 cm. long and 1 to 5 cm. in diameter. It is a perennial creeper, climbing to the summit of the highest trees, its branches putting forth roots which, reaching to the ground, initiate a fresh growth. Roots, stem, and leaves are equally in demand as a drug. The Indian pharmacopœia commends its use as a tincture (4 to 8 c.c. *in die*); as an extract (0·6 gram to 1 gram *per diem* in the form of pills); and as an infusion (1 : 10), of which 60 c.c. to 90 c.c. are to be taken thrice a day. The stems contain verberin, an uncrystallisable bitter substance, changed by dilute sulphuric acid into a glucoside, and a bitter kind of starch meal known as 'palo' (J. Soc. Chem. Ind. 6, 49).

GIN or **GENEVA** is a spirituous liquor made from spirit derived from grain and distilled with juniper berries and other flavouring substances. The term is a corruption of the word '*genièvre*' or '*junever*,' the French and Dutch equivalents respectively for *juniper*, which is the essential flavouring ingredient.

The principal varieties are the English, known as 'gin,' and the Dutch, described as 'Geneva,' 'Hollands,' and 'Schnapps.' The difference between them is chiefly one of flavour, and each manufacturer has his own special recipe, which is carefully preserved as a trade secret. The principal flavouring ingredients used besides juniper are angelica root, almond cake, calamus root, cardamom seeds, cassia buds, coriander seeds, creosote, liquorice powder, orris root, sweet fennel, turpentine, &c.

The grain used is almost invariably a mixture of maize, malt, and rye, the proportions being usually about 75 p.c. maize, 15 p.c. malt, and 10 p.c. rye for English gin, and about equal parts of each for the Dutch varieties, although sometimes maize is absent.

During the Napoleonic wars at the beginning of the last century, the use of corn, owing to its scarcity, was prohibited in the United Kingdom for the manufacture of spirit, and the manufacturers had recourse to molasses or low-grade sugar. This, however, produces a very inferior quality of gin, which is essentially a grain spirit, but it is still made, chiefly for exportation, by the addition of juniper oil or similar flavouring agent to the crude spirit.

In England, patent-still spirit is generally employed as a basis, but it is preferably not rectified so highly as to deprive it of the characteristic flavour of grain spirit. The flavouring ingredients are in some cases added directly or they are separately distilled and the distillate added to the spirit to be flavoured. Another and probably the best method is to redistil the spirit, after the addition of the flavouring ingredients, in a kind of pot-still with a long head or other simple rectifying arrangement.

In Holland, the manufacture is carried on mainly at Schiedam, where pot-stills are chiefly employed. The spirit is subjected to three or four rectifications, when it is known as 'moutwijn' or 'maltwine.' This is sold to the manufacturers of Geneva or Hollands who flavour it by methods similar to those above described for English gin.

The best '*Hollands*' is said to be prepared as follows: A mixture of two measures of ground rye with one measure of ground barley malt is mashed with about 24 gallons of water for each

cwt. of the mixed meal. The mashing being completed, the sp.gr. of the wort is reduced by cold water to between 1033 and 1038. It is then fermented, after which the whole is thrown into a still. To the first product of distillation, called *low wines*, a varying proportion of juniper berries with a little salt is added, and it is re-distilled. The spirit which now passes over is flavoured with essential oils or resins derived from the juniper as well as from the rye and barley used in brewing.

Sweetened gin (*e.g.* 'Old Tom' and 'Old Geneva') is made by the addition of sugar syrup to plain gin. The syrup is prepared by dissolving refined sugar in its own weight of pure water. Sometimes it is flavoured with orange-flower water, and is known as 'capillaire.' The clear solution is added in the proportion of about 6 gallons of syrup to 100 gallons of gin.

Plymouth gin is a special variety of gin made in Plymouth, and used extensively in the West of England. It has a characteristic flavour, said to be due to ether resulting from the addition of a little sulphuric acid to the spirit to be rectified.

The adulteration of gin, except by dilution with water, is not common. Alkaline carbonates, and sometimes alum and salts of zinc and lead, have been found. Juniper wood oil and turpentine oil are occasionally used as substitutes for or admixed with the oil from the juniper berry.

By the Sale of Food and Drugs Amendment Act, 42 & 43 Vict. c. 30, s. 6, gin may not be sold at a strength below 35 under proof, unless declared to be diluted. The percentage of water added may be found by multiplying the excess of degrees under proof beyond 35 by the factor 1·54. For example, a gin of strength 45 u.p. contains $10 \times 1{\cdot}54$, or 15·4 p.c. of added water over and above that present in gin at the minimum statutory strength of 35 u.p.

J. C.

GINGELLY or GINGILI OIL *v.* SESAMÉ OIL.

GINGER.

Description.—Ginger is the dried rhizome, either whole or ground to a powder, of *Zingiber officinale* (Roscoe), a plant 3 to 4 feet in height, which grows wild in India and China and is cultivated extensively in most tropical countries. At the present time, the chief kinds which find their way into the English market are Jamaica, Calicut, Cochin, African, Japanese, and in less quantity, Bombay. Japanese ginger is not derived from *Z. officinalis* and is therefore not *official* for medicinal purposes.

Preparation and properties.—The rhizomes are dug up when the plant is about a year old, washed, and dried in the sun. In some cases the epidermis is removed by scraping or cutting, in others the root is dried intact.

To meet the popular prejudice in favour of a white product various methods of treating the root are adopted. The commonest consists in immersion in milk of lime, when the coating of lime left after drying is of advantage in preventing the attacks of insects, fungi, &c. Gypsum and chalk are also used with a similar object. Ginger is also said to be bleached with sulphurous acid or bleaching powder, but most of the so-called bleached ginger has probably only been 'limed.'

The unscraped root has a yellow-brown wrinkled surface, while the scraped variety is smooth and nearly white. The pieces are, as a rule, from 2 to 4 inches in length, knotted and bent, flattened in section and with a short fracture.

On being cut with a knife, the best ginger presents a soft floury surface, inferior qualities appear hard, resinous, and shiny.

The chief structures observed when ground ginger is examined under the microscope are the starch grains, the vessels, reticulated, spiral, and scalariform, the sclerenchymatous cells, broad bast fibres with somewhat thin walls and occasionally thin-walled polygonal parenchymatous cells and oleoresin cells, which have escaped destruction during the grinding. The starch grains are, for the most part, elongated, simple (except in Japan ginger where aggregates of small granules occur), sack-shaped or oval, and vary in length from 12 to 50μ, the majority being between 20 and 30μ. The hilum is placed close to the narrow end and the striations are visible in the larger granules if properly illuminated.

Ginger is used as a condiment and flavouring agent and in medicine as an aromatic stimulant and carminative.

Composition.—Its chief characteristic constituents are a volatile oil to which the aroma is due; a fixed oil, gingerol, which gives the pungent flavour; starch and resin. The following figures (Richardson, from Leach, Food Inspection and Analysis, 446) will afford some idea of its composition:—

TABLE I.

—	Water	Ash	Volatile oil	Fixed oil and resin	Starch	Crude fibre	Albuminoids	Undetermined	Nitrogen
Calcutta	9·60	7·02	2·27	4·58	49·3	7·45	6·30	13·4	1·01
Cochin	9·41	3·39	1·84	4·07	53·3	2·05	7·00	18·9	1·12
Unbleached Jamaica . .	10·49	3·44	2·03	2·29	50·6	4·74	10·85	15·6	1·74
Bleached Jamaica (London) .	11·00	4·54	1·89	3·04	49·3	1·70	9·28	19·2	1·48
„ „ (America) .	10·11	5·58	2·54	2·69	50·7	7·65	9·10	11·7	1·46

Determinations by Garnet and Grier (Pharm. J. 1909, 83, 159-160) give the gingerol as from 1·1 to 2·2 p.c.

Adulteration.—The only form of adulteration to which whole ginger is subject is the addition of or substitution by ginger from which more or less of the strength has been removed by extraction with dilute alcohol or water, in the manufacture of ginger beer, &c.; or with strong alcohol for the preparation of the essence

or tincture. Ground ginger may be adulterated by the addition of foreign starches—wheat, maize, rice, turmeric; and in the past at all events, cayenne pepper and turmeric have been employed to restore the pungency and colour where these have been reduced by the practices already referred to.

Mineral matter, especially calcium carbonate and calcium sulphate, may also be present in excess, owing either to their deliberate addition or to the too liberal employment in the preparation of the article.

Detection of adulteration.—The detection of exhausted ginger in small proportion is at present impossible, and even when the amount is substantial, the problem is by no means an easy one, because the constituents which are removed by extraction with alcohol and water occur in widely varying proportions, even in different samples of the same kind of ginger, while, in the case of different kinds, the variations are still more marked. The following tables show this and also the changes in composition brought about by the processes of extraction as commercially carried out.

TABLE II.—RESULTS OF ANALYSIS OF 87 SAMPLES OF GINGER.
(Zeit. f. Untersuch. des Nahrungs u. Genuss. 1907, 14, 549.)

—	Water	Total ash	Soluble ash	Sand	Ether extract (volatile)	Ether extract (fixed)	Alcohol extract after ether	Light petroleum	Methyl alcohol extract
Highest . . .	13·85	9·33	4·51	3·79	3·08	8·08	4·46	5·77	9·58
Lowest . . .	9·20	3·24	1·52	0·05	0·90	2·84	1·12	1·95	3·82
Extracted Cochin . .	13·26	3·28	0·99	0·11	0·48	1·32	0·67	0·69	1·54
„ Bengal . .	13·42	4·52	1·93	0·97	0·46	1·18	0·55	0·54	1·90

TABLE III.
(Clayton, Analyst, 24, (1899) 123.)

—	No. of samp.	—	Water	Cold water extract	Ether extract	Alcohol 100 p.c. extract after ether	Light petroleum extract (fixed)	Ash	Soluble ash	Ash of cold water extract	Alkalinity of soluble ash (as K_2O)
Whole ginger .	11	max.	14·76	15·88	3·71	1·81	2·00	6·19	3·81	4·52	—
		min.	11·18	6·69	6·88	0·88	1·24	2·67	1·27	1·74	—
		mean	13·33	9·96	4·88	1·37	1·60	3·71	2·27	3·10	—
Ground ginger (commercial .	9	max.	11·83	15·40	9·37	1·21	3·57	6·47	3·48	3·84	0·33
		min.	10·39	4·54	4·42	0·41	1·43	2·05	1·43	1·72	0·13
		mean	11·32	10·36	6·18	0·81	2·11	4·50	2·46	2·96	0·24
Exhausted ginger	10	max.	12·07	14·06	4·33	1·07	1·49	2·70	1·13	1·90	0·15
		min.	11·05	2·57	1·79	0·69	0·10	1·41	0·43	0·61	0·04
		mean	11·62	7·89	3·20	0·77	0·76	2·06	0·49	1·08	0·09

The most useful determinations for the detection and estimation of exhausted ginger are the ash soluble in water, the alcoholic extract after extraction with ether, and the cold water extract, and these may with advantage be supplemented by the light petroleum extract or the methyl alcohol extract and a determination of the potash. Microscopical examination is of no assistance and the taste and smell of the sample are of limited utility on account of the great variations in strength of the different kinds of ginger.

No legitimate manufacturing operation affects the analytical results sufficiently to cause any trouble (Clayton, *l.c.*), but it must be borne in mind that the method by which the sample has been extracted, of which the analyst is usually ignorant, considerably affects the analytical results. (For the effect of exhaustion with alcohol of different strengths, *see* Liversedge, Pharm. J. 1896, ii. 112, and for information as to methods of extraction actually employed by ginger beer manufacturers, &c., *see* Analyst, 1893, 8, 200.)

The starchy substances likely to be added to ginger may be detected by the microscope. The unsymmetrical cross observed when ginger starch is viewed under polarised light distinguishes it at once from wheat.

Capsicum may be detected by the test suggested by Garnett and Grier (Pharm. J. 1909, 441), based on the fact that the pungent flavour of gingerol is destroyed by heating with alkalis whereas that of capsicum is not.

The United States Department of Agriculture has fixed the following standard for ginger: the starch (by diastase method) shall not be less than 42 p.c., the crude fibre not over 8 p.c., the total ash not over 8 p.c., the lime not over 1 p.c. and the ash insoluble in HCl not over 3 p.c. The Pharmaceutical Codex provides that the volatile oil shall be between 1 and 3 p.c., the ash between 3 and 5 p.c., and the aqueous extract not under 10 p.c. C. H. C.

GINGER GRASS OIL *v.* OILS, ESSENTIAL.

GINGER, OIL OF, *v.* OILS, ESSENTIAL.

GINGKOIC ACID $C_{23}H_{47}COOH$, m.p. 35°, is obtained from the fruit of *Ginkgo biloba* (Linn.) (Schwarzenbach, J. 1857, 529).

GIROFLE. *Dimethylphenoxylosafranine* (*v.* AZINES).

GLASS. Glass may be regarded as a solid solution of various silicates of indefinite composition, produced by the fusion of silica with two or more metallic oxides, the silica acting as the acid, or, more strictly speaking, the anhydride, and the oxide or oxides as the base.

Its dominating characteristic is an entire absence of any definite molecular structure such as is found in crystalline substances, and its mechanical, physical, and chemical properties are consistent only with the assumption that its molecules present the same indefinite arrangement as is found in liquids and colloid bodies. Vitreous substances are therefore characterised by the fact that there is no distinct boundary between the solid and liquid condition, the process of congelation of molten glass involving no critical change, but merely a gradual increase of viscosity until this becomes so great that the body behaves as a solid. It is this property of gradual stiffening which gives glass many of its valuable industrial properties; the lack of cohesion incidental to such a state accounts for its familiar property of brittleness.

A further characteristic of glass in general is transparency, but although this is one of its most valuable properties for the great majority of purposes, it is by no means universal, opaque and translucent glass being extensively used.

History. Glass of a crude type was known and employed in the arts at a very early period, but no reliable information as to its production and manipulation is available earlier than 1400 B.C. The method of preparing and working glass at this time is known with certainty from the discovery of remains of furnaces and workshops by Flinders Petrie at Tel-el-Amarna. The manufacture was confined to the production of rods and beads, and small vases formed by dipping a clay core into molten glass, working the surface into shape, and subsequently removing the core. The use of the blowpipe, which rendered the production of vessels of large size possible, was not discovered until considerably later—it was not, in fact, until the time of the Roman Empire that glass became an article of domestic and industrial use; but at the dawn of the Christian era the manufacture had been developed to an extraordinary extent; nearly every department of glass manufacture can, in fact, be traced back to this time.

Roman glass was almost invariably of the soda-lime type, rich in silica; the manufacture degenerated greatly in mediæval times, owing to the use of crude wood ashes, which produced a potash lime glass very low in silica and with excess of lime and magnesia.

It is probable, however, that the Venetians continued the Roman tradition of importing natural sodium carbonate (natron) for glass making, which enabled them to produce glass of finer quality, and may account to some extent for their pre-eminence in this art—the island of Murano being the chief centre of glass making throughout the mediæval period.

The earliest reliable record we have of the manufacture of glass in England dates from 1230, when we find the glass industry established on the border of Sussex and Surrey. This locality remained the sole centre of glass making in this country until the time of Elizabeth, when the restrictions on the use of timber for fuel caused its gradual decline.

The introduction of coal as a fuel resulted indirectly in the discovery of lead or flint glass, which was first manufactured in London, probably about the end of the seventeenth century.

The manufacture of glass was considerably hampered by Excise regulations until 1845, when the tax was removed. (See Excise Comm. Rept. 13, Glass, 1835.)

COMPOSITION.

The constituents of glass may be summarised thus:

A. Acids.
1. Silicon.
2. Boron.
3. Phosphorus.

B. Bases:
1. The $R_2'O$ group, Na_2O, K_2O;
2. The $R''O$ group, CaO, MgO, BaO, ZnO, MnO;
3. The $R_2'''O_3$ group, Al_2O_3, Fe_2O_3;
4. PbO (and occasionally Tl_2O).

C. Constituents occurring in coloured glass:
Metallic gold, silver, copper; carbon;
Sulphides of sodium and calcium;
Fluorides of calcium and aluminium;
Oxides of Co, Ni, Cr, Sn, Cu, U.

Simple silicates. Before considering mixtures of silicates, it is advisable to discuss shortly the properties of the simple silicates, a mixture of which forms glass. These may be roughly divided into two groups:

1. Those with a sharply defined melting-point and small viscosity, which are only stable in the crystalline state, and do not form glasses; the compound silicates of the lime and iron groups are of this type.

2. Those which have an indefinite melting-point, a viscous state intervening between the solid and liquid; in which the solidifying-point is lower than the fusion-point. These silicates form glasses, and comprise typically the alkali silicates.

Silicates of the alkalis.—These are the most fusible of all the silicates. By fusing silica with two or three times its weight of potash or soda, a homogeneous transparent mass is obtained, which dissolves completely in cold water. If the weights of silica and of soda and potash are equal, the resulting compound is still easily fusible, but it is no longer completely soluble. As the proportion of silica rises, the product fuses at an increasingly high temperature; these silicates do not crystallise even if cooled slowly.

Silicates of calcium and barium.—These silicates melt only at very high temperatures. The most fusible contain silica and base in such proportion that their oxygen ratio is 1 : 3; such a compound fuses at a red heat approaching whiteness. The resulting substance is crystalline when cold. With larger proportions of silica, complete fusion can be induced only at the temperature of the oxy-hydrogen flame. They are slowly attacked by water.

Silicates of alumina and of magnesia are generally present in glass as impurities. When pure they cannot be fused at a lower temperature than that of the oxy-hydrogen flame.

Silicates of iron and of manganese are often present in glass in small amount, either as impurities or to impart colour. They melt much more readily than the silicates of lime and baryta. Those with the formulæ $FeSiO_3$ and $MnSiO_3$ melt at a bright red heat. All of these crystallise if cooled slowly.

Silicates of lead.—These silicates fuse the more easily the more lead oxide they contain. The one of the formula $PbSiO_3$ melts at a bright red heat, and is somewhat yellow in colour. They crystallise only if cooled very slowly. On crystallisation the following compounds have been identified: $3PbO,SiO_2$; $2PbO,SiO_2$; $PbO,2SiO_2$; and PbO,SiO_2. The orthosilicate crystallises more readily than the metasilicate.

Mixtures of silicates melt at a lower temperature than the mean melting-point of their constituents, and often at a lower temperature than any one constituent. Those containing alkalis lose alkali by volatilisation if kept for a long time at a high temperature, and the melting-point rises. At the same time, mixtures of silicates are more stable than the simple silicates of which they are composed. When combined in proper proportions, a glass is formed which is, therefore, readily fusible, and, at the same time, only slightly attacked by water and acids.

Classification.—Taking into consideration the large number of substances available, and the fact that no definite proportions are necessary, a very wide range of glasses of different compositions is possible in theory.

In practice, however, the great majority of glasses may be referred to one or other of a few main types which may be classified thus:

A. Glass in which the acid is entirely silica, combined with two or more bases, one of which is an alkali.

1. *Soda-lime glass:* this type is very extensively employed for window glass, chemical glassware, bottles, &c. The precise composition varies in different cases, CaO is sometimes partially replaced by BaO, and a small amount of alumina is generally present.

(This type is generally referred to as 'crown glass' in scientific work, although this name properly signifies a particular process of manufacture.)

2. *Soda-lime-alumina glass:* this is chiefly used for beer, wine, and spirit bottles, owing to its strength and insolubility.

3. *Potash-lime glass:* generally known as Bohemian glass: used for hollow ware.

4. *Potash-lead glass* (generally known as 'flint' glass; in France it is known as 'cristal'). Used extensively in the manufacture of hollow ware, bottles, and optical glass.

B. Glass containing other acids in addition to silica:

1. *Boro-silicate 'crown'*: Type A1 with silica partially replaced by B_2O_3; used for optical glass, thermometer tubing, and laboratory ware.

2. *Boro-silicate 'flint'*: Type A4 with silica partially replaced by B_2O_3; used for optical glass, in the manufacture of enamels, 'strass' for imitation gems, &c.

3. *Phosphor glass*, in which the silicon is partially replaced by phosphorus.

C. Glass containing no silicon: 'borate' and 'phosphate' glasses are occasionally used in optical work.

D. Simple silicates, consisting of silica and alkali only. This type is soluble in water, and is known as soluble or water glass.

E. Quartz glass, consisting of pure silica in the amorphous state.

Table I. gives detailed analyses of some typical examples:—

TABLE I.

Type	——	Acid		R_2O		RO			Al_2O_3	Fe_2O_3	PbO	Misc.
		SiO_2	B_2O_3	Na_2O	K_2O	CaO	MgO	BaO				
A1	Roman sheet and hollow ware	69·0	—	17·34	0·59	7·09	1·11	—	1·89	0·87	0·70	—
	Table glass	70·4	—	9·13	8·66	10·00	—	—	1·51		—	—
	Baryta 'crown'	71·4	3·13	3·53	7·78	—	—	9·52	—		—	ZnO 4·5
	English sheet	72·0	—	13·00	—	13·00	—	—	2·0		—	—
	French sheet	71·9	—	13·10	—	13·60	—	—	1·4		—	—
	Plate	71·8	—	11·10	—	15·70	—	—	1·26	0·14	—	—
	Pressed glass	70·68	—	18·38	—	5·45	—	4·17	0·33	0·20	—	—
A2	Bottle glass	69·15	—	12·17	—	15·38	—	—	2·38	0·69	—	—
	Do. champagne	61·90	—	6·16	1·13	17·95	6·38	—	4·41	1·85	—	—
A3	Mediæval sheet	54·01	—	1·70	13·20	17·37	5·33	—	2·41	0·81	—	P_2O_5 4·18
	Bohemian ware	71·6	—	—	15·0	10·00	1·2	—	2·2	—	—	—
A4	Ordinary flint	53·17	—	—	13·88	—	—	—	—	—	32·95	—
	Dense flint	38·2	—	—	7·80	—	—	—	1·0	—	53·8	—
	Baryta flint	65·6	3·27	1·23	6·47	—	—	9·97	—	—	1·03	ZnO 12·2
	Fusible enamel	33·54	8·20	3·70	—	—	—	—	—	—	54·59	—
B1	Boro-silicate gauge glass	71·90	12·0	11·00	—	—	—	—	5·0	—	—	—
	Thermometer glass (Jena)	67·5	2·0	14·00	—	—	7·0	—	2·5	—	—	ZnO 7·0
	X-ray glass	39·6	30·0	10·00	—	—	—	—	20·0	—	—	As_4O_6 0·4
C	Phosphate crown	—	4·98	—	14·8	—	11·6	—	11·3	—	—	P_2O_5 56·6
	Borate flint	—	66·3	4·12	—	—	—	—	11·0	—	6·87	ZnO 12·6
D	Water glass	60·3	—	39·70	—	—	—	—	—	—	—	—

Rational formula.—As the bases differ in molecular weight, the percentage composition of glass does not immediately suggest its chemical relations; for some purposes it is more useful to compare the ratio of the oxygen in the silica to that in the bases. This is easily done by multiplying the percentage of each constituent by the proportion of oxygen in its molecular weight; the factors are: silica, 0·530; lime, 0·285; baryta, 0·104; lead oxide, 0·072; potash,

0·170; soda, 0·258; the total amount of oxygen in each group of bases is then found by addition, and its ratio to that in the silica determined.

Constitution.—The fact that powdered glass can be fractionated by means of elutriation or specific gravity solutions into portions of different density and composition, and that by surface etching with HF micro-crystalline structure can be developed, has led some observers to hold that glass is a homogeneous mixture of silicates rather than a solution. The great majority of facts are, however, only consistent with the view that it is a congealed solution. It has been shown, for instance, that the fusion-point is lower than that of a mixture of crystalline silicates of the same composition, and that the electrical conductivity decreases uniformly as molten glass cools, there being no break between the solid and liquid state, as in the case of crystalline silicates.

Coloured Glass.

Any of the types of glass considered may be produced in an endless variety of colours by the addition of a small quantity of one or more metallic compounds.

The same material does not produce the same colour in all glasses, the colour varying with the composition; the state of combination of the metal introduced also influences the colour produced to a considerable extent.

Coloured glasses may be divided into two classes:

1. Those in which the colour is introduced by a coloured compound of the metal in a state of solution in the glass; in this case the intensity of the colour is proportional to the concentration of the solution of colouring material.

2. Those in which the colour is due to the optical effect of minute particles held in suspension by the glass; here the colour depends upon the size and distribution of the particles.

Iron in the ferrous state produces a green colouration. Small quantities of iron are always found as an impurity unless special precautions are taken to exclude it, so that common glass is slightly green in colour, the colour being bluer in the case of potash than in soda glasses. If oxidised to the ferric state, the colour produced is yellow and of less intensity. About 2 p.c. of iron will produce a strong green or yellow colouration, according to the state of oxidation.

Manganese produces a range of colours from amethyst to violet, according to the composition of the glass; the full colour is only developed when the manganese is in a fully oxidised condition (Mn^{IV}), and can be altered or discharged by introducing reducing substances.

White glass containing manganese is often turned deep purple by prolonged exposure to actinic light, and, conversely, the colour of this purple glass can be discharged by heating to the softening-point. Manganese is frequently added to white glass to correct the slight green tint due to iron as an impurity, the colour produced by manganese being complementary to that of iron.

By adding manganese and iron together in considerable quantity, amber and brown glass is produced, and if the quantity is greater than the glass can dissolve, the excess remains in suspension, producing black glass.

Cobalt produces an intense colouration in all types of glass, 0·1 p.c. being sufficient to produce a strong blue, and a pale-blue resulting from even 0·01 p.c. The colour is very little affected by the composition of the glass or state of oxidation of the metal.

Nickel exerts a powerful colouring influence on glass, the colour varying considerably, however, with the composition of the glass and the state of oxidation of the metal. On account of the uncertainty in its action, nickel is not very much used in practice.

Chromium produces various tints of green, and is a very useful and extensively employed colouring agent, as, like cobalt, the colour is little affected by the condition of working.

Chromium is, however, only slightly soluble in glass, and if added to the extent of more than about 4–5 p.c. the excess separates out on cooling, producing an opaque green glass. It is possible, however, by careful manipulation, to get the oxide to separate out in the form of crystalline flakes; we then have a translucent green glass filled with minute spangles, known as *Chromium Aventurine* (comp. *Copper*).

It is said that a blue colouration can be produced with chromium in the case of glasses rich in barium and alumina.

Copper produces a wide range of colours. If fully oxidised, it forms soluble silicates which give an intense green or blue colour, according to the composition of the glass; but if added with a reducing agent, the copper can be precipitated in the metallic state, distributed as minute particles throughout the glass, which then becomes coloured ruby-red, owing to the reflection of light of shorter wave length than red by these minute particles.

It is a matter of some skill to obtain the right condition of division and suspension to produce this effect; if the particles become too large and unevenly distributed, a streaky opaque red is produced, resembling sealing wax, and known as *Hæmatinon*, whilst under certain conditions it is possible to obtain the particles of visible size, when they appear as minute spangles, producing what is known as '*Aventurine*' glass.

Gold forms colourless compounds with glass, but these are very unstable, and the gold can only be kept in solution by sudden cooling. If cooled slowly or if the rapidly cooled colourless glass is reheated to the softening-point, metallic gold is precipitated, and acts in the same way as the metallic copper described above, producing a fine ruby colour.

The ruby is more easy to obtain and regulate than in the case of copper, as there is not the danger of oxidation to contend with. The quantity of gold required is very small, 0·01 p.c. being the limit of solubility.

Silver acts in a similar manner to gold, but the particles transmit yellow light. The silver is readily absorbed by the glass, and this is taken advantage of to colour sheet glass yellow *by penetration*.

If glass be painted with any salt of silver and heated, the glass absorbs a certain amount of silver at about 400°, and, on further heating to about 800°, the compound so formed

decomposes, and the silver is precipitated, producing what is technically known as '*Silver stain.*'

The temperature of combination and precipitation varies with the composition of the glass, potash-lime glass low in silica producing the richest colour; with hard glasses the silver is not readily absorbed, and with some compositions it precipitates very rapidly, the particles assuming visible dimensions, with the result that the transparency of the glass is impaired, and in extreme cases a film of metallic silver appears on the surface.

Carbon. Glass is coloured yellow from suspended particles of finely divided carbides, produced by introducing carbon into the composition, in the same manner as by silver and gold.

Sulphur produces a greenish-yellow colouration by combining with the alkali and lime in the glass to form coloured sulphides. The addition of 7–10 p.c. of sulphur yields a black glass known as '*hyalithe.*' It is probably due to the formation of a trace of iron sulphide.

In the case of both carbon and sulphur the colouring effect only applies to those glasses free from lead, which would be thrown out of solution by reduction to metallic lead in the one case and sulphide in the other.

Selenium, which is closely allied to sulphur, produces colouration in the same manner, the colour produced being, however, a pale rose-red. The production of the colour depends, to a large extent, on the composition of the glass and the conditions of working; the replacement of calcium by barium greatly facilitates its formation.

Uranium produces a characteristic fluorescent yellow colour, especially in potash-lime glass, which is employed in the production of fancy glassware. With soda-lime glass the fluorescence is less marked, and it is not produced in lead glass.

Antimony in the form of lead antimoniate produces an opaque yellow colouration in the case of lead glasses only.

Table II. gives a summary of the application of these principles:—

TABLE II.

—	Potash-lime glass	Soda-lime glass	Lead glass
Iron Fe^{II} . .	Greenish blue	Bluish green	Yellowish green
„ Fe^{III} . .	Yellowish green	Greenish yellow	Yellow green
Manganese. Mn^{II} .	—	—	—
„ Mn^{IV} .	Amethyst	Reddish violet	Reddish violet
Cobalt . . .	Violet blue	Violet blue	Spectrum blue
Nickel . . .	Amethyst	Reddish brown	Purple
Chromium . .	Yellow green	Grass-green	Reddish green
Tin . . .	Opal	Opal	Opal
Copper Cu^{II} .	Pale blue	Greenish blue	Green
„ uncombined	Ruby	Ruby	Ruby
Gold, „ .	Rose-ruby	Rose-ruby	Rose-ruby
Silver, „ .	Orange	Deep yellow	Deep yellow
Carbon . . .	Pale yellow	Pale yellow	—
Sulphur . . .	Pale yellow	Pale yellow	—
Selenium . .	Rose	Rose	Rose
Uranium . .	Dichroic yellow	Yellowish green	Topaz
Antimony . .	—	—	Opaque yellow

These various elements may be combined together in a glass in almost any proportions to produce intermediate colours, and the range of colours available in modern practice is therefore practically unlimited, both in tint and tone. As with many solutions of coloured salts, the tint of a glass does not always remain the same where the glass varies in thickness, but varies in quality as well as in tone; cobalt blue glass, for example, in thin layers, transmits a considerable proportion of red light, which is absorbed by thicker pieces.

The colour of glass is, in many cases, modified by prolonged exposure to actinic light, radium emanation, and X-rays. Thus, Sir William Crookes has instanced (Proc. Roy. Soc. 74, 524) white table glass which has become deep purple by exposure to the sun in Chile, this being probably due to the oxidation of manganese in the glass.

Soda-lime glasses are coloured blue by radium emanation and X-rays, and potash-lime brown, whilst lead glass becomes cloudy.

Ancient window glass often becomes slightly opalescent, owing to the liberation of calcium phosphate on prolonged exposure to the sun, as this glass generally contains a considerable content of phosphorus.

Translucent, opal, and opaque white glass may be made by means of the following mixtures:—

Tin-enamel. Lead and tin are heated together; sometimes equal parts are employed, or as little as 15 parts of tin to 100 parts of lead. The metals oxidise, and the glass is produced by fusing together: sand 100 parts, pure potash 80 parts, mixed oxides of tin and lead 200 parts.

Arsenic-enamel. Sand 100, potash 16, lime 6, red lead 130, saltpetre ½, white arsenic 10 parts; or sand 100, red lead 200, potash 60, white arsenic 30 parts.

Calcium phosphate, or bone-ash, makes glass turbid and white; thus: sand 100, soda-ash 45, slaked lime 16, bone-ash 6, arsenious oxide 3 parts. A smaller proportion of bone-ash (2–4 p.c.) gives an opal glass. Such glass transmits reddish light. It may also be made, using red lead, thus: sand 100, potash 25, red lead 75,

bone-ash 8 parts. The addition of arsenious oxide to one of the above mixtures increases the fusibility while decreasing the transparency.

Fluorides also produce opacity. Glass rendered opalescent by them does not transmit red light, but is pure milk-white. A mixture giving good results is: sand 100 parts, red lead 32–35, potash 27–28, fluorspar 14–16. Cryolite may also be employed, but the glass is apt to devitrify owing to the excess of alumina introduced. The ordinary mixture consists of: sand 100, soda-ash 14·6, cryolite 14·6, chalk 6 parts. Sodium fluoride may be substituted, thus: sand 100, sodium fluoride (containing 10 p.c. of carbonate) 21, soda-ash 3, china-clay 10, and chalk 7 parts. Such opalescent glass is much used for lamp-shades, for thermometer scales, and for ornamental work. Another variety may be produced by aid of zinc oxide together with cryolite, thus: sand 100, cryolite 40, zinc oxide 10 parts. *Alabaster glass*, a substance which closely resembles alabaster in its translucency and surface, may be made by the following mixture: sand 100, soda-ash 42, asbestos 20, talc 20 parts.

Properties.

The two most valuable properties of glass, as already indicated, are:

1. Transparency.
2. Rigidity at ordinary temperatures, passing to plasticity at high temperatures.

This combination of properties is common to only a few colloidal substances, and vitreous materials are unique in possessing the further advantage of hardness and resistance to chemical change.

Physical properties. *Transparency.*—The great value of glass lies in the fact that it transmits practically the whole of the visual spectrum in equal amount; it does not, however, transmit the whole of the light falling on it, a certain portion is reflected at the surface of entry, and a further portion absorbed during passage through the glass. In the purest 'white' glass this absorption is very small, and practically uniform for rays of different wave length, as far as the visual spectrum is concerned, but is never entirely so; even the best glass, therefore, shows a slight colour when a considerable thickness is examined.

This selective absorption can be modified so as to produce coloured glass by varying the composition, as already described. Ordinary glass is to a large extent opaque to ultra-violet and infra-red light; this absorption varies a great deal, according to composition, being least in pure quartz glass, and greatest in glasses of high specific gravity containing lead, the latter being opaque to X-rays.

Special glasses are now made transparent to particular portions of the spectrum; thus UV glass is transparent far into the ultra-violet, whilst another variety is made so as to be opaque in this region, transmitting only the visual spectrum. Special glasses are also made for the transmission of X-rays (*see Table of analyses*).

The *optical properties* of glass are of great importance; reference is made to them below, under *Optical glass*.

Density varies with the molecular weight of the constituents, from 2·25 in the case of the lightest borate glasses to 6·33 in the case of the heaviest lead and barium glasses. The average for alkali-lime glass is 2·5, and for flint 3·0.

Mechanical properties. These have been very little investigated, although they are of considerable importance in special cases, such as large sheets of plate glass which have to withstand considerable wind pressure, and the gauge glasses of high-pressure boilers. The tensile strength of some special glasses measured by Winkelmann and Schott was from 2 to 5½ tons per sq. inch, and the crushing strength 3–8 tons per sq. inch.

The mechanical properties vary considerably with the composition of the glass, and also with the manipulation, more particularly the rate and conditions of cooling.

Hardness and resistance to abrasion is a property of great importance, but difficult to determine quantitatively, and no reliable data are available. It varies considerably with the composition; in general, it is directly proportional to the content of silica, lime, and alumina, and inversely to the content of lead and alkali; a high content of lead in particular reduces the hardness considerably. Soda glasses are in general harder than potash glasses. Hardness varies also with the process of working and is increased by rapid cooling and bad annealing.

Expansion varies considerably in different glasses. The mean cubical expansion of soda-lime glass is 0·000023 to 0·000027.

The relative expansion becomes of great importance when two different glasses have to be fused together, as in the case of flashed window glass and the decoration of glass by enamels, and also where glass has to be rigidly attached to metals, as in the case of electric lamps and enamelled iron ware. In most glasses the expansion is not uniform, and special glasses are now made for the construction of accurate thermometers where such a defect introduces serious errors.

Thermal endurance. The lack of power of withstanding sudden heating and cooling is one of the characteristic defects of glass, which limits its use in many cases. This is conditioned by a number of factors, chiefly by the low tensile strength and elasticity and the relation between the thermal conductivity and expansion.

The endurance is higher in glass rich in silica and low in lime and alumina, and is greatest in pure quartz glass, which is able to withstand extensive variations of temperature without fracture.

Coefficient of elasticity: flint glass: Young's modulus, $5{\cdot}5–6{\cdot}00\times10^{11}$; simple rigidity, $2{\cdot}3–2{\cdot}4\times10^{11}$; volume elasticity, $3{\cdot}4–4{\cdot}2\times10^{11}$; crystal: Young's modulus, $3{\cdot}4–4{\cdot}4\times10^{11}$; simple rigidity, $1{\cdot}2–1{\cdot}7\times10^{11}$; volume elasticity, $3{\cdot}5–4{\cdot}4\times10^{11}$. These are in the C.G.S. system of units. *Velocity of sound* in glass, $4{\cdot}5\times10^{5}$. *Mean specific heat* between 0° and 100° =0·1770; between 0° and 300°, 0·1900. *Conductivity for heat*, 0·0005–0·002. *Resistance* (electrical) at 200°, $2{\cdot}27\times10^{16}$; at 300°, $1{\cdot}39\times10^{14}$; at 400°, $7{\cdot}35\times10^{13}$ (Everett's Illustrations of the C.G.S. System of Units).

Chemical properties. Glass is characterised by being exceedingly stable and chemically

inert at ordinary temperatures; this is a determining factor in its use for very many purposes.

The chemical resistance is, however, by no means perfect, and is dependent on the composition, and more particularly on the content of alkali; it may be considered in general that a glass containing over 15 p.c. of alkali is not suitable for any purpose where chemical stability is of importance.

Special glasses are now prepared to meet the stringent requirements of chemical laboratories, &c., as regards stability. In general it is found that the boro-silicate crown glasses prove the most suitable for this purpose, and more particularly those containing zinc and a minimum of alkali.

The resistance of glass to atmospheric influence is a matter of great industrial importance. This action is a very complex one, involving attack by water, alkalis, and acids combined with constant variation of temperature and mechanical abrasion.

Several methods have been proposed for determining the resistance of a glass to attack. The most useful is that proposed by Mylius, in which the glass is exposed to the action of water for a definite period, and the amount of action determined by means of an ethereal solution of iodo-eosin, which is turned pink by the liberated alkali; the intensity of the colour thus produced, measured by a colorimeter, expresses the degree of resistance. The results obtained by this method, although not agreeing with practical experience in all cases, give a very good indication of the weather-resisting qualities of different glasses (*see* Mylius, Zeitsch. anorg. Chem. 1910, 67, 200).

The loss of weight on treatment with water or with N/1HCl, under given conditions, is also employed as a means of giving information on this point.

Action of water on glass. Pure water attacks all glass by extracting the alkali to a certain extent; in the cold, the action is negligible except with very poor glass. The action increases with rise of temperature, and superheated water becomes an active corroding agent.

Ordinary Bohemian glass heated with distilled water in an autoclave to a temperature of 300° is entirely decomposed in 2 hours, the alkali being extracted, and a skeleton of calcium silicate in the shape of the original glass remaining. The action of water on glass is enhanced by the fact that all glass is, more or less, hygroscopic; this property increases rapidly with an increase in the content of alkali.

Hydrolysis. In addition to acting on the surface of glass, water may also cause a change of constitution by penetrating and combining with the glass, probably forming hydrates with the silicates present. This action frequently takes place with glass exposed to continual damp at ordinary temperatures.

Glass which has been buried for a prolonged period shows this change; thus Hausmann has found 19 p.c. of combined water in a specimen of decayed Roman glass; the writer has found that ancient window glass, which has been attacked in this way, whilst showing no apparent change, has become so modified in constitution that the bases can be entirely extracted by cold dilute hydrochloric acid, leaving a skeleton of silica in the form of the original glass.

Alkaline solutions attack glass more energetically than water; they act by first combining with the silica, thus setting free the bases, which are dissolved or removed by the water, exposing a fresh surface of glass for attack.

Dilute acids have relatively little action on glass, much less than pure water; strong acids have practically no action, except in the case of glasses of the type in which silica is partially replaced by boric or phosphoric acid. The only exception to this rule is hydrofluoric acid, which rapidly decomposes all types of glass by combining with the silica to form gaseous fluorides; highly basic glasses are less readily attacked than those rich in silica.

Devitrification. If glass is maintained for any length of time at a temperature corresponding to the freezing-point of any of its constituent compounds, these will tend to crystallise out from solution; when glass becomes crypto-crystalline in this manner, it is said to devitrify. The facility with which this happens depends on the composition of the glass; glasses rich in lime and alumina devitrify very readily, whilst those rich in alkali or lead can be maintained at the critical temperature for a considerable time before the crystallisation takes place. When the composition of the glass is such as to favour the formation of silicates freezing at a temperature at which the glass is sufficiently liquid to allow free motion of the molecules, devitrification takes place readily, and such a glass can only be maintained in the amorphous state by rapid cooling from the temperature at which crystallisation commences to that at which the glass becomes sufficiently rigid to prevent molecular movement.

In the trade, glass in which devitrification has taken place is known as 'Ambitty.' Devitrification is sometimes artificially induced, as in the case of 'ambitty sheet,' a sheet glass used for decorative purposes, which is crypto-crystalline, containing microscopic crystals of lime and aluminium silicates.

The chemical behaviour of glass at high temperatures has to be taken into account by the manufacturer in connection with the construction of the melting pots; a glass rich in silica will dissolve bases from its surroundings, whilst, on the other hand, glasses rich in base attack any acid material with which they come in contact; the denser lead glasses, especially those containing boron, for example, corrode very rapidly the fire-clay pots in which they are melted.

Manufacture.

Materials employed. *Silica.* The principal source of silica is sand. Only the purest varieties of white sand are suitable for modern glass making, as ordinary sand contains iron, which imparts a greenish-yellow colour to the glass.

In ancient times colourless glass was almost unknown, on account of the use of such impure sand. In the 17th century ground flint was employed as the source of silica, in order to get over this difficulty (hence the name 'flint glass'), but its use is now entirely abandoned, as deposits of sand of exceeding purity have

been exploited. The sands of Fontainebleau and Lippe, for example, analyse 99·98 SiO_2.

Glassmakers' sand is obtained in this country from Lancashire, where it forms shallow beds of great extent, lying close to the surface, and from Bedfordshire, where the strata vary from 40 to 50 feet in thickness. Sand from Lynn on the east coast is also largely used.

For window glass sand containing ½ p.c. of iron oxide may be used; but for crystal and plate glass only a trace is permissible. The effect of iron may be neutralised to some extent by addition of oxide of manganese. In Bohemia, quartz is pulverised by heating it and dropping it into water, and subsequently grinding in wooden mortars with quartz pestles.

For coarse bottle glass, common sand containing as much as 2 p.c. of iron may be used.

Alkali. The Romans used natron, a native sodium carbonate, as the source of their alkali; the Venetians, the ashes of a marine plant known as kali. In the north of Europe and in this country, the ashes of inland vegetation, notably beechwood, were employed as a substitute, a very impure potash-lime glass being thereby produced.

The use of sodium carbonate was reintroduced on the discovery of the Le Blanc process for producing it from salt, which cannot itself be used as a source of alkali, as silica will only react with it at a temperature above its boiling-point.

In 1825 the French began cautiously to substitute sodium sulphate for carbonate, the former being a cheaper material. In 1831 English manufacturers followed their lead, and at present sodium sulphate is largely used. The sulphate must for this purpose be freed from all traces of iron by means of lime. In employing sodium sulphate it is customary, but not essential, to add carbon in the form of anthracite coal, or charcoal, to deprive the sulphate of its oxygen. This is only possible with glass free from lead. It must, however, be noted that, although sodium sulphate costs only about half as much as carbonate, 71 parts of the former are equivalent to 53 parts of the latter, and, moreover, the sulphate requires a much higher temperature to react with the silica than the carbonate. In adding carbon, it is advisable to reduce the sulphate not to sulphide, which would colour the glass yellow, but to sulphite.

Potash is invariably employed as carbonate, generally known as pearl-ash; in the manufacture of strass it is rendered caustic, and purified by treatment with alcohol.

In lead glass and certain of the coloured glasses a portion of the alkali is introduced in the form of nitrate. These compounds are employed essentially for their oxygen contents, to obviate any tendency to reduction.

Lime is generally introduced in the form of carbonate or hydrated oxide, the source being chalk or limestone. The former is contaminated with flint particles, which are only objectionable if of a large size, when there is a danger of the silica remaining undissolved, producing opaque enclosures in the finished glass, technically known as 'stone.'

In the case of limestone the impurity to be guarded against is magnesia, which tends to make the glass hard and viscous. In certain special glasses, however, a small content of magnesia is intentionally introduced.

Barium is introduced in the form of precipitated carbonate, the barium wholly or in part replacing calcium. For every 100 parts of calcium carbonate 197 parts of barium carbonate must be substituted.

Alumina is generally present in small quantity in glass as an impurity, owing to the solvent action of the glass on the fire-clay vessels in which it is prepared. In the hard glasses, where alumina forms an essential constituent, it is, however, added to the mix in the form of hydrate. In opal glasses it is added in the form of cryolite; this substance is, however, primarily used on account of its fluorine content.

Manganese. This is essentially a colouring oxide, but it is largely employed in the production of white glass to correct the colouration produced by iron, as already described. It is generally added as MnO_2 in the form of pyrolusite.

Cullet. In addition to the materials already described, broken glass, or 'cullet,' is invariably added. The object of this addition is to use up the numerous fragments of glass left over during the operations of manufacture; and, what is of still greater importance, to cause the materials employed to react on each other at a lower temperature than they would do if melted together alone; in fact, to serve as a flux. At the temperature necessary to produce action between the silica and the other constituents of the glass, the alkali is volatile, and much is lost before it reacts with the silica. But the cullet melts, and dissolves both alkali and silica, thus promoting their interaction. While it is stated that lime glass deteriorates if often remelted, probably owing to the volatilisation or some of the alkali, the makers of lead glass find that an improvement results by frequently breaking up the glass by ladling it into water and remelting it (this is termed to 'dragade').

The manufacturers of flint-glass bottles for perfumery and other purposes, as a rule, use no batch at all, preparing their glass entirely from cullet with the addition of the necessary metallic oxides in the case of coloured glass; there are cullet merchants who collect the broken glass from hotels, &c., for this purpose.

Mixing. It is of the utmost importance that the constituents of glass should be thoroughly mixed. This is achieved in some works by hand, a workman turning over the powdered materials with a wooden shovel and passing them through a sieve until they are completely incorporated. Usually, however, a mechanical mixer is employed. A convenient form of mixer consists of a hollow drum with blades disposed like the floats of a paddle, revolving in a box, of which the lower half has a cylindrical section. It has been recommended to mix the constituents in a wet condition, employing some of the enormous amount of heat which is wasted in all glass furances, for the purpose of drying them after they have been thoroughly incorporated.

Proportions of constituents of glass. It is impossible to do more than indicate the proportions in which the various ingredients of glass are mixed. A great deal depends on the temperature of firing the length of time which the

pot is exposed at different temperatures, and the amount of cullet mixed with the batch. Within certain limits, each manufacturer exercises his own judgment. An analysis of the finished glass throws little light on the amounts of the raw ingredients used. For if sodium sulphate be employed, a considerable proportion is removed by skimming, inasmuch as not all the sulphate enters into reaction with the silica. Again, a not inconsiderable proportion of alkali is lost by volatilisation; and, lastly, the composition and quantity of cullet present must be a factor.

Tables III. to V. (abridged from Die Glasfabrikation, by W. Stein) show how much glass may be theoretically produced from given constituents, allowing for loss as skimmings, or, as it is termed, 'glass gall,' and by volatilisation of alkali. The figures must be taken as merely approximate. Section A shows the proportions of raw constituents in the batch; section B, the loss of various constituents; and section C, the weight of glass obtainable from 100 lbs. of batch. Here the addition of cullet would, no doubt, considerably modify the results, as well as the temperature of the furnace and the duration of the firing.

Containing vessels. In order to convert the mixed material into glass by fusion, containing vessels of refractory material and a specially constructed furnace are required.

Pots.—The manufacture of these is, as a rule,

TABLE III.—POTASH-LIME GLASS.

—	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII
A—Batch												
SiO_2	100	100	100	100	100	100	100	100	100	100	100	100
K_2CO_3	50	60	50	34	35	66·75	70	60	50	52	40	42
$Ca(OH)_2$	15	20	—	15	—	—	20	CaO 10	—	—	18	—
$CaCO_3$	—	—	20	—	26	33	—	—	22·5	11	—	17·5
As_4O_6	0·25	0·5	1·5	—	—	1·66	1·66	—	0·25	—	—	—
KNO_3	—	1	1·5	—	—	6·66	6·66	—	1·5	—	—	—
MnO_2	—	—	0·05	0·33	0·5	0·2	0·2	—	1·5	0·5	—	—
Smalt	—	—	—	—	—	0·05	0·05	—	—	—	—	—
B—Loss												
K_2O	5	6	6	4	4	8	8·5	6	5	5	4	4
CO_2	14	17	25	11	23	36	22·5	17	24	20	11·5	19.5
Glass gall	5	6	—	—	3·5	—	—	6	5	5	4	4
As_4O_6	0·25	0·5	1·5	—	—	1·66	1·66	—	0·25	—	—	—
N_2O_5	—	0·5	0·75	—	—	3·5	3·5	—	0·75	—	—	—
C—Percentage of glass												
	85 p.c.	83 p.c.	82 p.c.	90 p.c.	81 p.c.	76 p.c.	82 p.c.	83 p.c.	80 p.c.	81 p.c.	87 p.c.	82 p.c.

Of these the first five are for potash crystal; Nos. 6 and 7 for Bohemian mirror-glass; Nos. 8, 9, and 10 for Bohemian hollow glass, for white bottles, &c. No. 11, Bohemian combustion tubes; and No. 12, Bohemian plate glass.

TABLE IV.—SODA-LIME GLASS.

—	I	II	III	IV	V	VI	VII	VIII	IX	X	XI
A—Batch											
SiO_2	100	100	100	100	100	100	100	100	100	100	100
Na_2CO_3	33·3	62·5	34	30	35	—	—	—	—	—	6
Na_2SO_4	—	—	—	—	—	44	50	44·6	32	30	35
CaO	14·3	—	—	—	—	6	—	—	—	—	—
$CaCO_3$	—	7·5	14·5	35	40	—	20	18	45	30	30
Coke	—	—	—	—	—	3	3	3	2	3	3
MnO_2	0·16	0·25	0·25	0·25	0·25	—	—	—	—	—	—
As_4O_6	—	0·2	—	0·2	0·2	—	—	—	—	—	—
B—Loss											
Na_2O	3	5·25	3	5	3	3	3	3	2	2	3
CO_2	12·5	27	18·5	27	30·5	—	9	8	19·5	13	15·5
Glass gall	3·5	6·25	3·5	3	3·5	2	2·5	2	1·5	1·5	2·5
As_4O_6	—	0·2	—	0·2	0·2	—	—	—	—	—	—
SO_3	—	—	—	—	—	23	27	23·5	17	16	18
C—Percentage of glass											
	87 p.c.	77 p.c.	83 p.c.	79 p.c.	79 p.c.	82 p.c.	76 p.c.	78 p.c.	78 p.c.	80 p.c.	78 p.c.

No. 1 is for French mirror glass; Nos. 2, 3, 4, and 5, French plate glass; and the remainder for plate of second quality.

TABLE V.—BOTTLE GLASS, AND LEAD-POTASH GLASS.

—	I	II	III	IV	V	VI	VII
A—Batch							
SiO_2	100	100	100	100	100	100	100
Na_2SO_4	—	25	—	—	—	—	—
Coke	—	3	—	—	—	—	—
Basalt	50	5	—	—	—	—	—
Wood ashes	160	—	—	—	—	—	—
$CaCO_3$	—	34	—	—	—	—	—
Pb_3O_4	—	—	66·6	60	55	70	42
K_2CO_3	—	—	33·3	20	36	26	33·3
As_4O_6	—	—	—	—	1	—	—
KNO_3	—	—	—	—	—	3·3	16·6
MnO_2	—	—	—	—	—	—	0·5
Borax	—	—	—	—	—	4	—
B—Loss							
Na_2O	8	2	—	—	—	—	—
K_2O	—	—	2	1	2	1·5	2
Glass gall	20	3	—	2	—	—	—
N_2O_5	—	—	—	—	—	1·5	8
CO_2	50	15	10·5	6	11·5	8·5	10·5
O	—	—	1·5	1·5	1	1·5	1
SO_3	—	12·5	—	—	—	—	—
As_4O_6	—	—	—	—	1	—	—
C—Percentage of glass							
	75 p.c.	80 p.c.	93 p.c.	94 p.c.	92 p.c.	93·5 p.c.	89 p.c.

Nos. 1 and 2 are receipts for coarse bottle glass; the remainder for lead glass. In all the last cullet is added, but its influence has not been taken into consideration.

undertaken by the glass manufacturer. It is necessary that they should withstand a temperature of about 1000°C. for many months, and hence they must be made of very refractory fire-clay. *Fire-clay* consists essentially of aluminium silicate; that employed for the purpose in England comes from Stourbridge; in France, from Forges-les-Eaux (Seine Inférieure); and in Germany, from Ardennes (Belgium) and from Klingenberg. An idea of the composition of the clays can be gathered from the following analyses:—

—	No. 1	No. 2	No. 3	No. 4	No. 5
Silica	71·6	64·2	71·7	57·4	68·0
Alumina	26·0	32·2	22·3	38·0	29·0
Ferric oxide	1·2	2·4	4·5	1·8	0·2
Lime	0·1	—	0·5	1·8	—
Alkalis	1·1	1·2	—	1·0	0·8
	100·0	100·0	99·0	100·0	98·0

No. 1 clay, from Forges-les-Eaux; No. 2, from Ardennes; No. 3, from Stourbridge; No. 4, from Klingenberg; No. 5, from Bohemia.

The proper clay to use in a particular case depends on the kind of glass to be made. All clays are attacked, more or less, by the molten glass, but it is essential, not only that the composition shall be such as will combine very little, but also that the dissolution shall be uniform; if it is attacked in an irregular manner, there is a danger of particles of undissolved material contaminating the glass in the form of 'stones.'

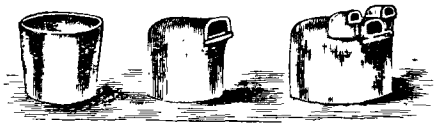
All clays in their natural state contain water, varying from 6 to 20 p.c. During firing, this water is expelled, and the pot contracts considerably. As the clay in its pure state would contract too much on firing, a quantity, usually one-fifth of the weight of the clay, of the material of old pots freed from adhering glass and finely ground, is mixed with it.

The mixture is subjected for some time to a kneading process known as 'treading,' which is done by the feet of the workmen. Attempts have been made to introduce mechanical kneading appliances, but it is said to be impossible to produce satisfactory pots by this means.

The clay is then preferably left for many months to mature. This doubtless has for its object the combination with the clay of water present as such; it renders the clay more plastic. Abroad, pots are made with help of a mould; but English manufacturers consider that better results are obtained with hand-made pots. A slab of wood or stone is sprinkled with a thin layer of sand, and, beginning at the middle of the bottom, the workman constructs a spiral of clay, each piece being thoroughly kneaded with the hand and incorporated with the clay previously laid down. Scratches are then made in the first layer, and a second layer is laid, still proceeding spirally, on the top of the first, until a sufficient thickness of clay has been accumulated for the bottom of the pot. Then the sides of the pot are built up in a similar manner, adding small rolls of clay and pressing them into the portions already laid, always proceeding spirally. The utmost care is taken that the whole structure is solid, and that the clay does not enclose air. Several crucibles are kept in hand at one time, so that one may have an opportunity of setting while the workman is engaged at another.

Figs. 1 to 5 give an idea of the various forms of pots in use for different purposes:—

FIG. 1. FIG. 2. FIG. 3.



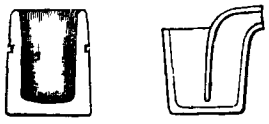


FIG. 4. FIG. 5.

Fig. 1. Open pot used for alkali-lime glasses.

Fig. 2. Covered 'dog-house' pot for lead glasses which have to be protected from contamination by particles of carbon or reducing gases.

Fig. 3. The same with shoulders for small pots ('dandies') for coloured glass.

Fig. 4. Section of open pot for plate glass, with channel for lifting.

Fig. 5. Section of pot with division for continuous working.

After the pots have been made, they are left for a time, varying from 3 to 12 months, at the ordinary temperature, or in a gently warmed room. A stock of pots is always kept so as to replace any casualty without delay.

In working, a circular or oval ring of fire-clay is generally floated on the glass to keep back any impurities, the glass being gathered from the centre of the ring.

Tanks. Where glass has to be prepared in very large quantities, the Siemens furnace is used, in which the glass in contained in a huge tank, instead of pots; this has the advantage of continuous working, fresh material being fed into one end as the glass is withdrawn from the other.

These tanks are built of large blocks of fire-clay, and their construction requires at least as much care as that of a crucible, as they have to resist the action of molten glass for a very much longer period. Tank furnaces are very much cheaper in operation than pots, but it *is not* possible to produce glass of such fine quality in them.

Construction of furnaces. The furnaces in which the glass is melted have also to be constructed of highly refractory clay to withstand the continuous intense heat. Fire-clay alone is not always refractory enough, and bricks composed of pure silica, obtained from Dinas, Valley of Neath, Wales, are employed for the crown or vault of Siemens furnaces. For the ordinary furnace, fire-clay alone, or clay mixed with pebbles broken up into irregular fragments by being heated and quenched in water and then ground, is made use of. It is found that this material, owing to the angular form of the particles, causes the clay to bind together better than if sand were used. The bricks are not fired before the furnace is built; but they are dried, and during building they are made to adhere together by rubbing the brick to be added against those already laid. The adhesion of the dry clay is so considerable that very flat-domed or arched roofs can be constructed without any centering. While clay contracts during heating, bricks containing silica expand slightly, and a furnace constructed with the latter requires less patching after the temperature has been raised. It is obviously of the utmost importance, when open glass pots or a tank is used, that no droppings from the roof should enter the pots or tank, else the glass becomes 'stony,' owing to the presence of small unfused particles.

Although it is advisable to construct the domes or vaults of a furnace of silicious bricks, the bed of the furnace must be made of bricks more basic in character, otherwise the glass, which occasionally runs over them when a pot breaks, would corrode them and render them useless.

In some cases the necessity of specially shaped bricks for the dome of the furnace is avoided, by building up the dome-shaped part with moist clay by hand, after the circular walls have been laid in the same manner as pots are made. The disadvantage of this plan is that the furnace must lie unused for many months before it can be fired, in order that the clay may dry. It is, therefore, never resorted to in this country. Moreover, the clay contracts on firing, and the cracks have to be repaired before the furnace is fit for work.

As regards the principles of construction and arrangement, glass-making furnaces may be roughly classed into two types:

1. Those in which the fuel is burnt in the furnace itself; this is the oldest and simplest type, and is still in use for many purposes.

2. Regenerative and recuperative furnaces, in which the process of combustion is carried out in two stages, a combustible gas being first produced by partial combustion in a 'gas producer,' which gas is then burnt in the furnace; these are of modern introduction, the principle being first applied to glass making by Siemens.

Although in the direct type of furnace the whole of the calorific power of the fuel is generated in the furnace itself, whilst in the indirect type a certain amount is lost in the initial combustion, the latter method is more efficient for the following reasons:—

1. The gaseous state of the fuel enables considerable economy to be effected by transferring the heat of the waste chimney gases to the fuel; this is the principle of regeneration.

2. The composition of the gaseous fuel can be readily controlled so as to obtain the maximum heating effect with certainty.

Fig. 6 gives the general arrangement of the direct type of furnace.

As the fuel itself must not come in contact with the glass pots, the fire-box is placed below the furnace, and entrance for the stokers is through an arched passage, A (Fig. 6). The fuel is small coal or gas coke. The flames and products of combustion pass through a short vertical shaft, C, into the body of the furnace, striking against the vaulted roof D, by which they are deflected downwards towards the sides of the chamber, heating the pots E. They escape through the short flues F, one of which is situated between each two pots, so that in a furnace with twelve pots there are twelve flues. The entrance from the chamber into the flues is

at the bottom of each; and they pass through the side of the vaulted roof, and deliver into the wide open stack G. It is of importance that smuts and smoke should not enter the furnace, especially when open pots are employed; and

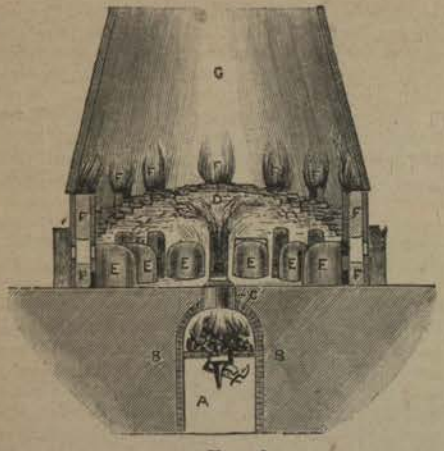


FIG. 6.

the stoking of the furnace must therefore be regular and constant.

Various appliances for mechanical stoking have been applied to glass furnaces, similar in principle to those employed in other industries.

Siemen's regenerative furnace. The essential feature of this is that the fuel is supplied to the furnace in a gaseous state from a gas producer (for construction of gas producers, *see* article FUEL).

The regenerative effect is obtained in one of two ways.

1. A large chamber filled with loosely stacked fire-brick is constructed at each end of the

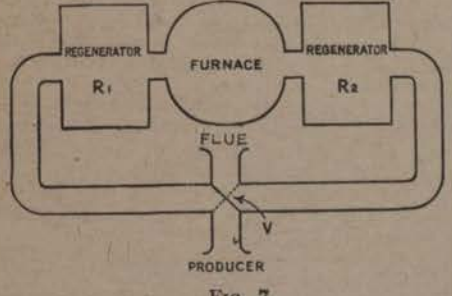


FIG. 7.

furnace (R_1 and R_2), and connected with the chimney stack and gas producer, as indicated in Fig. 7. At regular intervals the valve V is reversed, and the fuel gases then enter the furnace through the chamber R_2 instead of through R_1, as previously (or *vice versâ*). Considerable heat has been absorbed by the bricks in this chamber from the escaping furnace gases, which is transferred to the fuel gases, and the chamber R_1 is now heated up in the same way to give up its heat to a further portion of fuel when the valve is again reversed.

2. The furnace gases pass away through channels in fire-clay blocks, the incoming fuel gases passing over the exterior of these blocks and taking up the heat from the walls of the tubes. This is generally known as 'recuperation,' to distinguish it from the first method.

The regenerative principle may be applied to pot furnaces, the regenerators taking the place of the hearth and stoking appliances; more characteristically, however, it is applied to the heating of the tank furnaces referred to above. The diagrams below illustrate the construction of a furnace of this type.

Fig. 8 shows a cross-section of the furnace;

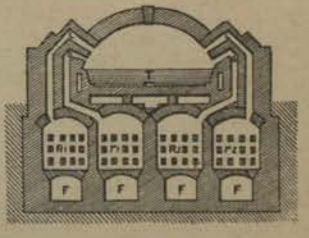


FIG. 8.

the regenerators R and r are seen below the furnace, with their 'ports' L and G conveying the heated gas and air respectively to the open tank, whilst below again are the flues F, with which are connected the valves regulating the direction of the current. T is the fire-brick tank in which the glass is contained.

Fig. 9 is a longitudinal section of the same furnace, showing the tank with the flue ports at the sides. The raw materials are introduced at the opening A, and the finished glass is withdrawn for working at the other end, B.

The tank is divided into compartments by floating partitions, P_1 and P_2, which ensure that the glass travels slowly from one end to the other as its fusion progresses, and that only refined melt reaches the working end.

The arched way C is known as the 'cave,'

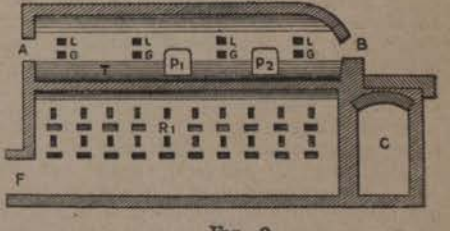


FIG. 9.

and provides a means of access to the regenerators for purposes of repair.

Various forms of *electric furnace* for glass manufacture have been introduced, the main principle being that of a tank to contain the mix, through which a current is passed by means of electrodes at either end, the glass being fused by the heat developed by its resistance (*see e.g.* Sauvageon, Four électrique pour la fabrication du Verre, Paris, 1905).

The process of preparing the glass. In the case of pot furnaces, the first operation is to

prepare the pot, which, for this purpose, is gradually heated in a subsidiary furnace called a 'pot arch,' until it attains the temperature of the main furnace, this process taking a matter of several days. A pot is always kept ready in the pot arch in this way whilst the furnace is in operation, so as to be ready to immediately replace any of the working pots that may break.

The operation of replacing a broken pot by a new one in this way is known as 'pot setting,' and is a very arduous process requiring great skill.

This 'setting' having been accomplished, the pot is then filled up with the batch, and the furnace kept at the highest temperature so as to hasten the reaction, and also to render the glass thereby produced as fluid as possible, so that the carbon dioxide and other gases evolved may escape, leaving the glass free from bubbles. In this connection, it may be noted that, although it is of advantage to have the batch in a state of fine division for the sake of facilitating the reaction, this must not be overdone in the case of the silica, otherwise there is a danger of minute air bubbles being left in the glass on the solution of the particles which are difficult to eliminate.

When the process of fusion is complete, the surface of the glass is generally found to be covered with a scum, generally known as 'glass gall.' This consists of impurities and various materials which have not entered into combination. Its composition may be seen from the following figures :—

—	Window glass	Glass for table purposes	Bottle glass
Sodium sulphate	83·32	90·51	55·92
Calcium sulphate	10·35	6·00	25·11
Salt . . .	1·43	0·04	0·20
Glass, clay, &c. .	3·35	3·30	17·77

This matter is removed by means of a ladle. If, as in some cases, a fire-clay ring floats in the pot, it is only necessary to skim off the gall from the interior of the ring. The quantity of this uncombined material has been, however, reduced to an almost negligible quantity by modern improvements in accurate mixing of the batch and in the regulation of the heating.

When the glass has been thoroughly melted and refined and is ready for working, the temperature of the furnace is allowed to fall until the glass attains sufficient plasticity to be worked.

Manipulation. The various methods of manipulating the molten glass into shape may be divided into three broad classes.

1. *Blowing.*—The initial stage in this method of working is that known as 'gathering,' which consists in collecting a quantity of the molten glass on to the end of an iron tube by dipping this into the pot or tank. This 'blowpipe,' with its adherent glass, is then removed from the furnace, and the glass allowed to slightly stiffen. The rod is then again dipped into the pot to gather a further quantity of glass, this process being repeated until the desired amount is obtained, which will vary, of course, with the nature of the article to be produced.

The 'gathering' is then rendered symmetrical in shape by gently rolling it over the surface of an iron block technically known as 'marver,' and is then formed into a hollow sphere or flask by blowing into the pipe. From this rudimentary shape the various types of blown glass are evolved by a series of manipulations which vary very widely in different branches of manufacture.

2. *Casting.*—In this method a mass of glass is removed from the furnace either by lifting the pot bodily and turning its contents on to an iron table, or by inserting an iron ladle into the glass and emptying the contents of this in the same manner. The latter method has, however, many objections, and is only rarely employed. The mass of glass thus obtained is then worked into shape by means of rollers.

3. *Pressing.*—Here a mass of glass, obtained either by 'gathering' on a solid rod instead of a blowpipe, or by pouring or ladling, is forced into a mould by a plunger.

In many branches of manufacture these methods are modified and combined, and, as the details of working vary very widely according to the article to be made, it will be more satisfactory to give further particulars in discussing the production of the various varieties of glassware.

Annealing. Whatever be the nature of the object prepared, if the glass, after manipulation, is allowed to become rigid quickly by cooling off in the open air, it will be found to be in state of strain, owing to unequal cooling of different portions, and is liable to fly into pieces spontaneously or if jarred. To obviate this, all glass articles, as they leave the hands of the workmen, are subjected to a process of slow and uniform cooling.

This is performed by passing them through a long tunnel technically known as a 'lear,' heated at the entrance to a temperature just below the softening-point, the temperature falling gradually from this point until at the other end the glass emerges at the ordinary atmospheric temperature.

The glass articles are stacked on trays linked together by an endless band, and as each tray is filled, it is pushed forward into the lear, the trays thus following one another down the tunnel at a speed depending on the rapidity with which each tray is filled.

The Uses of Glass.

Only a brief outline can be given here of the principal branches of glass manufacture, which may be classified thus :

1. Window glass.
2. Bottles.
3. Optical glass.
4. Hollow ware.
5. Quartz glass.
6. Soluble glass.

1. Window glass. All the methods of manipulation indicated above are employed in the production of the flat sheets of glass of varying character which are grouped together under this heading, because the proper term, 'sheet glass,' is restricted by custom to a single variety. We can divide the different types primarily into :

(*a*) Blown ;

(*b*) Cast or plate.

In each case a soda-lime glass is generally used ; typical analyses are given in Table I.

(*a*) *Blown window glass.* What is known in the trade as 'sheet glass' is generally made by a process the main outlines of which are indicated in the diagram (Fig. 10).

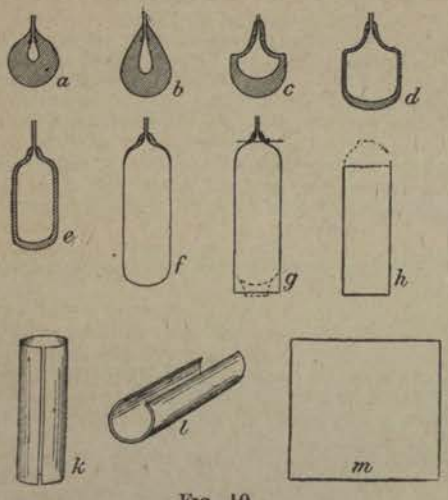


FIG. 10.

The glass is first gathered as already described (*a*). The next stage of the process consists in a preliminary blowing of the mass so obtained (*b*, *c*, *d*), aided by mechanical devices, so as to bring it into the shape of a sort of flask with a shoulder just beyond the end of the pipe, which determines the diameter of the cylinder which will ultimately be produced. The flask is enlarged by repeated blowings, the blowpipe being at the same time swung round through a semicircle, much as a stick is swung in one's hand, under which treatment the flask, which is kept in a softened condition by constant reheating, elongates itself by its own weight, and by this means ultimately a long narrow cylinder is produced (*e*, *f*). When this has been developed to its full size, the end is heated in the furnace, and either blown or cut open and manipulated until the soft glass opens out to form a true continuation of the rest of the cylinder (*g*). The glass is now removed from the blowpipe, and the other end of the cylinder cut off or opened out in a similar manner to the above, and it then assumes the shape of an open cylinder like a lady's muff (*h*).

The completed cylinder, or 'muff,' is now allowed to cool, and is then laid in a horizontal position, and cut along its entire length by drawing a heavy diamond skilfully down the inside surface (*k*).

The split cylinder is now flattened in a special furnace. Here the cylinder is laid with its split edge upwards on a perfectly smooth stone, and heated to the softening-point, when it commences to unroll (*l*); it is then smoothed into a flat sheet (*m*) by the aid of a 'polissoir,' or rod of iron, tipped with a flat block of wood, kept moist to prevent its burning. In modern works various mechanical appliances are employed in this process.

The finished sheet is now pushed forward through an opening into the annealing chamber, and when sufficiently rigid it is placed on its edge along with others previously flattened. When the chamber is full, the fire is extinguished, and the sheets are allowed to cool for several days. They are then removed from the furnace and sorted according to quality and thickness. The latter is generally expressed by the weight per square foot, the standard weights being 15 ozs., 21 ozs., 26 ozs., and 32 ozs.

The quality of the sheets so produced varies very widely, the defects incidental to the complicated process of manufacture being numerous. The principal defects are 'stones,' or opaque enclosures which cause liability to cracking; the presence of bubbles of gas, which is known as 'seediness'; excess of colour due to impure materials; 'stringiness,' due to lack of homogeneity in the glass.

The commonest and most serious defect is due to the difficulty of getting the sheet perfectly flat, with the resulting formation of irregular hollows and bulges which cause distortion of objects seen through it. The best sheet glass is never perfectly free from such distortion, and it is always possible to identify it by examining the surface by reflected light. These defects are, however, eliminated in *patent plate*, which is selected sheet glass with the markings and defects removed by grinding and polishing to a plane surface, in the same manner as plate glass.

Fluted sheet, largely used for office partitions, &c., is a variation made by blowing the cylinder at its final stage of dilatation, and before opening out the ends, into a metal mould marked with the fluting.

Various glasses are produced in a similar manner which are utilised in decorative work under fancy names, such as Muffled, Venetian, &c.

Sometimes also the glass is intentionally allowed to devitrify during the working, to produce the 'ambitty sheet' referred to under *Devitrification*.

Coloured or tinted sheet is also produced for various purposes. Sometimes the glass is coloured throughout, and is then known as *pot metal*, but more frequently the colour is only a thin veneer on one surface of colourless glass. This is known as '*flashed glass*,' and is prepared by first taking a small gathering of the coloured glass on the blowpipe and covering this with larger subsequent gatherings of white. In the formation of the 'muff,' the colour is thus distributed in a thin and even layer on the inside surface of the cylinder.

Crown glass. This method of preparing sheet glass was universally employed from the 17th to about the beginning of the 19th century, when the method just described, which enables larger sheets to be produced at less cost, superseded it.

The process starts in the same way as the last, with the production of a hollow sphere (*a*, *b*), Fig. 11, but at this stage a rod, or 'ponty,' is attached to the base of the sphere by means of a lump of the molten glass (*c*). The blowpipe is now detached by cracking off the neck of glass attaching to it, leaving the glass an open flask attached to the ponty (*d*). This is then held in front of a special furnace, with the ponty held horizontally, and rapidly revolved (*e*), when, under the influence of centrifugal force, the

softened glass expands into a flat disc, with a boss (known as a 'bullion') in the centre (*f*).

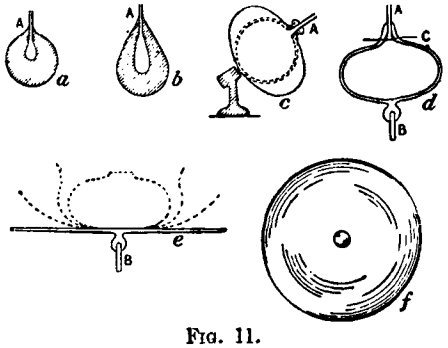


FIG. 11.

Such 'tables of crown glass are produced up to 52 inches in diameter, which is, however, an exceptional size. It is not economical to cut squares from crown glass larger than about 12 × 18 inches, but for special purposes sheets up to 20 × 18 inches are occasionally seen. The great waste in cutting renders this glass expensive, so that its use has been practically abandoned, except for purposes where its superior polish and freedom from surface markings outweigh these disadvantages. Its chief use at the present time is for the preparation of microscope slides. (It should be noted that the name, 'crown glass,' originally applied to this *process of working*, is now often applied to any soda-lime glass with reference to its *composition*.)

Various devices have been suggested for producing sheet glass by mechanical means, to avoid the laborious and costly blowing process. Some of these processes are in actual operation, but the difficulties attendant upon them have not as yet been overcome to the extent of making mechanical sheet glass a serious rival to the manual process. The general aim of such devices is to obtain the glass direct from the furnace in a thin sheet, either by letting it flow through a narrow slit or by dipping an iron bar into the glass along its entire length and slowly raising it; the great difficulty to be overcome is the tendency for the glass ribbon so produced to contract by surface tension into a rope before it can be cooled.

(*b*) *Cast window glass* or *plate glass*. This is made, as already indicated, by casting the glass on a flat table and rolling it out into a sheet. The best plate glass, suitable for polishing is prepared in pot furnaces, as the glass has to be of the best quality, free from every trace of impurity. The form of crucible used for melting the glass is shown in Fig. 4. The table is constructed of iron plate or of phosphor bronze. It has been found that, if made in one piece, it acquires the form of a flat arch, owing to the greater expansion of the upper surface when the hot glass is poured on it; hence it is made in segments, so that, although each segment expands, the whole table acquires the form of a number of flat arches, and less glass is lost in grinding than would be lost if the arch were a single one. The table is placed close to the door of the furnace, and it is arranged to run on rails, so that it can be brought opposite to any one of the openings through which a pot is removed. On the other side of the table is the annealing furnace. The pot, having been taken out of the furnace, is caught by tongs attached to a crane, lifted above the table, and tilted so that the contents are poured on to one end of the table in front of a manual roller by means of which the plastic glass is flattened into a sheet. The thickness of the plate is adjusted by causing the edges of the roller to run on rails as guides, the height of which above the level surface of the table may be altered at will. After it has cooled sufficiently to become stiff, the plate is transferred to the annealing furnace and gradually cooled.

This forms the 'rough plate' from which the finished article is produced by an elaborate process of grinding and polishing. For this purpose the plate is fixed to a table by means of plaster of Paris. This table revolves on a central axis, and arms project over it, to the ends of which cast-iron rubbing plates are attached. These plates also revolve, and by means of screws their position can be shifted so as to bring them when desired near the centre of the table or near its circumference. The surfaces of the glass are first ground off flat and parallel by means of a coarse abrasive which leaves it with a matt surface, which is then reduced to a smooth surface by finer and finer abrasives. The final operation of polishing is carried out by means of a similar machine, the rubbers of which are, however, covered with felt and fed with rouge and water.

In this process of grinding and polishing, the plate loses about one-third of its original weight, the amount depending on the perfection with which the rough sheet is cast; it is, therefore, of the utmost importance that it should be prepared as nearly flat as possible, otherwise the labour of reducing it to a plane surface becomes excessive.

Polished plate is produced in very large sizes, 25 feet by 15 feet being not uncommon.

The *rough rolled* glass used for roofing and similar purposes is prepared in much the same way as the rough plate just described, only cheaper material is used, and little care is taken to eliminate impurities. Instead of pot furnaces, the cheaper tank furnaces are employed, the glass being removed to the casting bed by means of a huge ladle, which is dipped into the tank and swung out by means of a crane.

Figured rolled glass, having a pattern impressed on one side, is prepared either by cutting the pattern on the bed, or preferably by 'double rolling.' In this method no bed at all is employed, but the glass is first fed between two plain rollers, and the sheet so formed is finished by passing between a second pair of rollers, one of which bears the pattern.

Armoured plate is the latest triumph of plate-glass manufacture. It consists of rough, polished, or figured plate in the substance of which wire netting is embedded during the process of rolling. This glass is now extensively used for roofing and other purposes, as in case of breakage by fire or otherwise the wire netting holds the fragments of glass together and prevents the entire collapse of the sheet.

2. **Bottle glass.** As a general rule, the first consideration in the production of bottles is

cheapness, so that waste products are utilised as far as possible as materials, and the cheapest and crudest methods of working are employed.

In the case of bottles to contain liquid under pressure, the mechanical strength of the glass has to be considered, whilst it must also possess sufficient chemical stability to withstand the action of corrosive liquids for a long period.

On all these grounds the alkali content is kept as low as is consistent with fusibility, and a considerable percentage of iron is admitted, as this assists fusion, the colour incidental to its use not being material in the majority of cases. The RO group is kept high, barium and magnesia being often present in considerable amount, whilst the alumina content may be as much as 10 p.c. In the case of the cheapest class of bottle, natural alkaline rocks are sometimes employed as raw material, and blast-furnace slag is also utilised, the molten slag being in this case conveyed to the tank and reduced to the proper composition by the addition of alkali and sand. For the better classes of bottles materials of greater purity must, of course, be used. Bottles for perfumery and similar purposes are largely manufactured from flint glass on account of the greater brilliancy and ease of manipulation. In some works flint-glass cullet is used entirely as the raw material.

In some cases tank furnaces are employed for the manufacture of the larger and commoner bottles used for beverages, &c., but in general pot furnaces are used.

The process of production is invariably that of blowing. A pear-shaped flask is first produced on the blowpipe in the manner already described, which is then brought to the shape of the body of the bottle by blowing into the interior of an iron mould, the top of which is made to open and close by means of a pedal so as to allow the flask to be inserted and the moulded bottle to be withdrawn. The bottle is then transferred from the blowpipe to a ponty in a similar manner to that described under crown glass, leaving the neck free. This is reheated and moulded to shape by means of the tool shown in the diagram (Fig. 12). By inserting the plunger inside the neck, the dies, which are cut to the shape the neck is to take, can be brought together by grasping the arms C, and the neck is brought to the required finish by revolving the bottle against the mould thus formed. Large bottles generally have their necks 'cast on,' a small gathering of glass being added after removing the blowpipe and moulded into shape by special tools.

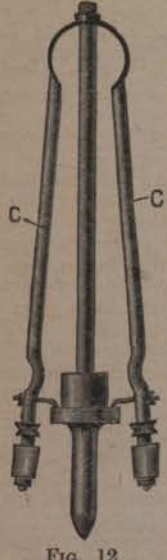


FIG. 12.

Bottles made in this manner generally show seams corresponding to the joints in the mould; these are obviated by the improved process known as *spinning*. In this case the gathering is inserted in the mould in the usual way, but the blowpipe is revolved during the blowing. A splinter of wood is placed in the mould before insertion of the glass, which, being ignited by the glass, covers the surface with a slight deposit of carbon, which exerts a polishing action on the glass during the spinning. Very highly finished bottles with no trace of mould marks result from this process, which, however, requires great skill in operation.

Many improvements have been introduced in recent years with the object of eliminating the manual operations of blowing and producing the bottles entirely by mechanical means. Various machines for this purpose are now in operation, the bottles being produced direct from a solid gathering of metal by a combination of mechanical pressing and blowing by compressed air with the aid of various moulds, the whole being worked by machinery, and attended only by a gatherer, an operator to control the levers, and a boy to transfer the finished bottles to the lear.

Bottles of large dimensions, such as carboys, were formerly blown by 'hand,' the lung power of the blower being assisted by injecting water during the blowing, and using the expansive force of the steam so generated. Compressed air for blowing, and various mechanical devices for relieving the workman of the weight of the glass, are now employed.

Glass tanks and similar vessels of very large size are prepared by the process introduced by Sievert. The glass is cast and rolled out into a sheet on the surface of a perforated iron plate. The sheet of glass is clamped down all round the edge of the plate, which is then turned over, so that the glass hangs from below, and compressed air is injected through the perforations, which distends the sheet into a suitable mould placed below. (For an account of this process, *see* Progrés récentes dans l'industrie du Verre, Le Mois Scientifique, 1903.)

3. **Optical glass.** The manufacture of glass for lenses and optical instruments differs widely from those branches already discussed, both as regards the composition of the glass and the methods of manipulation.

Composition.—The action of glass on light varies very greatly according to its composition, and in order to secure different optical effects, a large number of glasses of exceptional nature are prepared.

The principal optical constants which determine the use of a particular glass are:

1. Refractive index for the D line (μ_D);
2. Mean dispersion for C–F (Δ);
3. Relative dispersion for different portions of the spectrum;
4. Ratio between refraction and mean dispersion, expressed by the formula $\nu = \frac{\mu_D - 1}{\Delta}$.

The refractive index of glass is roughly proportional to the density, whilst the dispersion varies with the composition, being lowest in boron and phosphorus glasses, and those containing a high content of the RO group.

The two main types of glass used in optical work are those containing lead, which have both refraction and dispersion high, and a low value for ν; and alkali-lime glasses, in which both are low, but the dispersion is low as compared with the refraction, and ν is consequently high.

In optical work these two types are known as 'flint' and 'crown' respectively.

In general, the value of ν is inversely proportional to the density; by the use of barium, however, which combines a high density with the chemical nature of the RO group, it is possible to obtain a third type, having a high index of refraction, but very little dispersion, and consequently a high value for ν.

A still higher value of ν can be obtained by the use of phosphate and borate glasses, whilst the use of thallium oxide, in partial replacement of lead, results in a glass of exceptional density and refractive power.

The optical qualities can theoretically be varied to a large extent in this manner, but in practice the range is severely limited by the necessity for chemical stability. On the one hand, glasses too rich in such substances as barium readily devitrify, which prevents the slow cooling essential to homogeneity and freedom from stress, and, on the other hand, the exceedingly dense flint glasses, which are free from this defect, are readily corroded and decomposed, and also combine readily with the crucible in which they are melted, with resultant modification of their composition and properties.

Borate and phosphate glasses are so unstable that their use has been abandoned, except in lens systems which allow of their being cemented between more resistant glasses.

The optical constants of a few typical examples of modern optical glasses are given in the following table :—

Make	Type	μ_D	Δ	ν	Sp.gr.
Jena O. 225	Phosphate crown	1·5159	0·00737	70·0	2·58
Jena S. 30	Barium phosphate crown	1·5760	0·00884	65·2	3·35
Jena O. 144	Boro-silicate crown	1·5100	0·00797	64·0	3·45
Chance	Hard crown	1·5179	0·00860	60·2	2·46
Chance	Barium crown	1·6065	0·01046	57·9	—
Jena O. 114	Soft crown	1·5151	0·00910	56·6	2·55
Chance	Light flint	1·5472	0·01196	45·8	—
Jena S. 57	Dense flint	1·9626	0·04882	19·7	6·33

Preparation.—In order that the optical effects of the glass may be uniform, it is of the utmost importance that the glass should be as homogeneous as possible, and free from striations caused by difference of density. In the case of lenses it is also of great importance to reduce the absorption of light to a minimum by having the glass as nearly colourless as possible.

In order to conform to these conditions, the very greatest care is taken with all stages of the manufacture; the raw materials are, in the first place, very carefully selected and purified, and are then mixed as intimately as possible. The mixture is then introduced into covered pots, similar to those used for flint glass, only with the mouth prolonged into a funnel. The furnaces are of special construction, each containing a single pot. When the pot has been filled by repeated and gradually diminishing charges of the batch, and the whole has become molten, the temperature is raised until the glass becomes sufficiently liquid for the bubbles with which it will then be contaminated to escape. In some of the best optical glasses it is, however, found impossible to obtain sufficient fluidity to discharge the last traces of bubbles, and lenses formed of such glass characteristically contain a few small air-bells here and there.

When this process is complete, the glass gall on the surface of the glass has to be entirely removed preparatory to a thorough and laborious stirring to ensure perfect homogeneity. The pot and its contents are then allowed to cool down, at first as rapidly as possible, until they have become rigid in order to prevent any tendency to separation into layers of different density. When the glass is sufficiently set to obviate any danger in this direction, however, the subsequent cooling to atmospheric temperature is conducted as slowly as possible, in order to secure perfect annealing.

The pot is then broken and removed from the glass by chipping, and the resultant mass of glass is broken up and the pieces carefully examined for defects. The best pieces are then reheated to the softening-point and moulded into the slabs or discs supplied to the optician, to be subsequently ground into shape and polished. This is done in a similar manner to plate glass, being first roughed into shape by a coarse abrasive and an iron shape, smoothed with finer and finer abrasive, and finally polished with rouge until it accurately fits a pattern shape.

Lighthouse prisms. It will be readily understood that the laborious process of preparing optical glass renders it expensive, and the difficulty of preparing it of uniform quality in large blocks is enormous.

The cost of the large lenses required for lighthouses and searchlights would be quite prohibitive if made by this method, and as they are merely required to concentrate rather than accurately focus the light, such refinement of production is unnecessary. They are prepared, therefore, by melting the glass as carefully as possible, and casting it into iron moulds shaped roughly to the prisms required. The blocks so produced are then ground to shape and polished in the manner of plate glass.

Strass, or *paste.* This is a variety of optical glass used for the manufacture of artificial gems (the name is derived from Strasser, who first employed special glasses for this purpose).

It is a dense lead glass having the highest refraction that can be obtained without undue softness of the glass. The manufacture is similar in the main to that of optical glass on a very much smaller scale. The rough glass obtained from the melting is carefully sorted, reheated, and shaped up in moulds and then cut into the form of brilliants. Coloured pastes are

also prepared to imitate rubies and emeralds, and black opaque glass to imitate jet.

Enamels for the decoration of metal are of similar composition to optical flint, but usually contain a very high percentage of boron, which increases the fusibility and makes them adhere better to the metal, and also enables better colours to be obtained by the addition of the various colouring oxides described above. Such enamels are prepared by fusing the raw materials in a crucible, and, when melted, pouring the contents out on to an iron slab. Instead of removing the crucible from the furnace for pouring, it is preferable to have a hole in the bottom, closed by a plug, the contents being then discharged on to the plate, placed below the furnace, by removing the plug.

4. Hollow ware. This term embraces all the infinite variety of articles used for table service and decoration, laboratory glassware, fancy vases, lamp shades, and so forth.

Table and *fancy glass.* In this country a light flint glass is usually employed for this purpose, as it has greater brilliancy than lime glasses.

The glass is made in a great variety of colours, different colours being often combined in one article either by 'flashing,' blowing two portions of an article separately in different colour and then welding together, or by winding threads of coloured glass round the object whilst it is plastic.

The various articles are all derived from the simple flask which is the starting-point of all blown goods, the production of the various shapes being a fine art, the glassblower producing most elaborate designs by dexterously manipulating the plastic glass with the aid of a few simple tools.

As with fancy sheet glass, various moulds are used in combination with the blowing, to regulate the shapes and produce various designs on the surface.

Compressed air and mechanical contrivances for reducing the labour of production are also largely employed in modern works, and the simpler and more largely used articles, such as tumblers, are now in some cases prepared entirely by mechanical means in a similar manner to bottles.

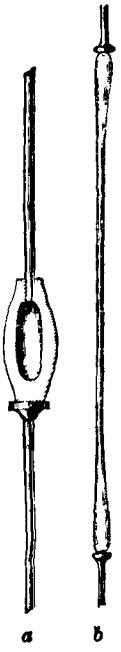
Articles produced by moulding in this way, however, are only suitable for cheap work, as, on account of the chilling of the surface by the moulds, they lack the finish and polish characteristic of hand-made goods.

A large variety of hollow ware is also made at the present time by *pressing* instead of blowing. Simple shapes of such pressed ware are produced by forcing the glass into a mould by means of a plunger; but more complicated shapes are now produced by using two moulds to press the two halves of a complicated shape, and then welding the two halves together whilst they are still plastic. Cheap articles, such as water jugs, are prepared in this way.

Considerable power is required in order to obtain a sharp impression, and glass manipulated in this manner has to be of a somewhat different composition to blown ware, as it must be plastic over a shorter range of temperature in order to secure a perfect impression of the mould; that is to say, it must be very mobile when hot, but quickly attain rigidity on cooling. This is attained by reducing the RO content to a minimum, a soft flint glass or a mixed alkali-lime glass low in lime being employed.

Laboratory glassware is produced in a similar manner to table glass as regards manipulation, but greater care has to be taken in the composition and manufacture of the glass, as it is required to be as little affected as possible by water and acids and to have the greatest possible thermal endurance. Soda-lime glass is employed for the generality of articles, but a number of special glasses are made: the Jena Geräte glass is designed specially for analytical work, having a maximum resistance to corrosion by boiling solutions.

Glass tubing and rod or cane. Rod is produced from a solid gathering by attaching a working rod to the end of the lump, previously rolled on the marver, and extending it by drawing apart the two rods. For tubing, the gathering is expanded into a thick-walled bulb before the mass is extended (Fig. 13, *a*, *b*).



a *b*

FIG. 13.

For thermometer tubing, in which the bore is elliptical, the gathering is slightly expanded, and, after being squeezed flat on the marver, a fresh gathering of metal is taken on, rolled to a cylinder, and then drawn.

Variegated cane may be produced by inserting a mass of molten glass into a mould which contains round its inner surface, in a perpendicular position, a number of short lengths of coloured canes. These adhere to the molten mass, which is then withdrawn and marvered. Some more glass is gathered from the pot to cover the coloured cane, and the whole mass may then be drawn; by *twisting*, spiral patterns may be produced. As glass retains the form given to it in the lump, even after drawing, varieties of cane may be made by moulding the first metal, preferably coloured, then covering it with molten glass, and then drawing it into cane.

The cane may be drawn to any desired degree of fineness by heating it before a blowpipe and spinning it on a wheel. Such fine glass is used for embroidery, and even woven into a fabric. It is also employed, under the name of 'glass wool,' for the purpose of filtering liquids which would attack ordinary filtering materials.

Glass tubes of large calibre are sometimes prepared by *pressing*, a cylindrical mould being used, which is closed at one end by a plunger several millimeters less in diameter than the interior surface. The mould is placed with its open end vertical, the lower end closed by the plunger, on which the mass of glass is thrown. As the plunger rises the glass is distributed in the annular space left between the plunger and the inner surface of the mould.

The composition of glass used for the production of tubing varies according to the

purpose for which it is to be used. Tubing for laboratory blowpipe work is required to be fusible and to be free from tendency to devitrification, a soda-lime glass rich in alkali is therefore employed. For combustion tubing, requiring to stand a high temperature, on the other hand, an alkali-lime glass rich in lime is used.

The special 'resistance' tubing manufactured at Jena is prepared from a boro-silicate glass containing zinc and magnesia. A similar glass is prepared for thermometer tubing to obviate the aberration of the zero point common to thermometers prepared from ordinary glass.

Glass beads.—1. *Hollow.* These are produced by blowing small bulbs out of glass tubing, plain or coloured. The interior is filled with coloured wax; or if pearls are to be imitated, with 'pearl essence'—*i.e.* the small scales of whitebait and similar fish, ground to an impalpable powder, and preserved in ammonium chloride solution. 2. *Solid* or *Venetian.* These are either cut from thick-walled coloured tubing by means of a guillotine cutter, and to round the sharp edges, heated to redness in a revolving drum, when the edges melt. To prevent adhesion, and the closing up of the perforation, they are kneaded in moist clay, or in a mixture of clay and finely ground charcoal before heating. They are finally polished by shaking in bags with bran. Opaque beads, like mother-of-pearl, are produced from tubes drawn from glass which has been violently stirred so as to inclose minute air bubbles, which in the process of drawing are elongated into parallel canals. Long beads are termed bugles. Large ornamental beads are made by taking the glass from the pots with a slightly conical rod covered with fine china clay. By holding the rod vertically, the glass slips down the rod, and by revolving the latter, the spherical form is secured. The rod is allowed to cool, and the bead knocked off when solid. A certain amount of ornamentation can be produced by twisting coloured glass round the bead while it is still hot; or by placing small drops of coloured glass on the hot bead. Glass marbles are made from coloured glass rod; it is cut off in lengths, and these are heated in a revolving drum, china-clay or talc being present to prevent adhesion. The rotatory motion causes them to assume a globular form.

5. **Quartz glass** is composed of practically pure silica in the amorphous state, and is prepared by fusing quartz or sand. As the temperature of fusion is much higher than is obtainable in ordinary glass furnaces, its production has only been rendered possible by modern advances in the production of high temperatures, more particularly by the introduction of the electric furnace.

Until quite recently, quartz glass was an article more of scientific interest than industrial use, but during recent years great strides have been made in its production, and it has now become an important factor, not only in the production of articles for laboratory purposes, but also for the construction of industrial plant.

Two varieties are now on the market:

1. *Transparent.*—Resembling ordinary glass; this is prepared from quartz in a furnace heated by means of oxy-hydrogen. It is only made in comparatively small sizes for laboratory work. Flasks, crucibles, and beakers are supplied, and tubes and rods of various calibre, which can be easily worked up into various forms of apparatus, using an oxy-hydrogen flame in the ordinary blowpipe. The glass is also spun into fine threads suitable for replacing glass wool for filtering purposes.

2. *Non-transparent.*—This is prepared on a much larger scale by the fusion of glassmakers' sand in an electric furnace, so arranged that the sand forms its own containing vessel, as no crucible can be obtained to withstand the necessary temperature. The opacity is due to the numerous air bubbles disengaged during the fusion, which it is impossible to eliminate, as sufficient fluidity cannot be obtained to effect their escape, both on account of the high temperature required and also because silica commences to boil at a temperature only a little above its fusion-point. In the process of working these bubbles are drawn out into long parallel tubes, giving the material a characteristic silky lustre (*cf. Opaque beads* described above). This material is adapted for the preparation of beakers, evaporating basins, retorts, tubes, &c., which are now manufactured in very large sizes, a capacity of several gallons being not uncommon.

This silica glass is chiefly valuable on account of its great thermal endurance, due principally to its low coefficient of expansion; it can be plunged while red hot into water without fracture. It can also withstand temperatures up to 1200°C. without alteration, and is, therefore, eminently suitable for combustion tubing and so forth. On prolonged exposure to a temperature above 1200°C., however, it devitrifies, reverting to crystalline tridymite.

Its chemical stability is very great, and it withstands the action of all boiling acids (except HF); on the other hand, being highly acid, it readily combines with all basic materials, and a vessel in which heated alkali or metallic oxide is placed rapidly disintegrates.

This material also has very nearly the hardness of quartz, and is therefore greatly superior to glass in resistance to scratching and mechanical injury.

Quartz glass also forms a perfect insulator, being free from the hygroscopic tendency of ordinary glass; an electroscope mounted on quartz will remain charged almost indefinitely. On this account, and by reason of its great elasticity and freedom from elastic fatigue, it is very valuable for the construction of physical instruments. For the suspension of galvanometer mirrors extremely fine threads are prepared by fusing small globules of silica, which are attached to a sort of miniature cross-bow, and drawn out to a great length by shooting the bolt.

The transparent material has the valuable optical qualities of natural quartz without the drawback of double refraction, notably great transparency to the ultra-violet end of the spectrum. For this reason it is used in the construction of the mercury vapour lamp. If it could be prepared in large pieces free from striations and bubbles, it would prove very valuable in lens construction. The index of refraction (μ_D) is 1·554.

6. **Soluble or water glass.** This is not a true glass, but an alkaline silicate, prepared by

fusing sand with either potash or soda, or by heating soda and infusorial earth under pressure. A simple silicate is thus formed, which has the appearance of glass, but is capable of being dissolved in water to a viscous solution resembling treacle. When the proportion of alkali exceeds 50 p.c., the solution can be prepared by boiling the vitreous mass in water, but with glasses richer in silica superheated water under considerable pressure is required. When the content of silica exceeds a certain point, which corresponds approximately with the formula $Na_2O{\cdot}3SiO_2$, it is found impossible to prepare a satisfactory solution, the excess of silica separating out.

The solution so prepared is used for a large variety of purposes. It is an essential ingredient in the preparation of fireproof cements and lutings for jointing fire-brick, &c. These can be made to set hard in the cold by the addition of lime, which causes the precipitation of gelatinous silica, the joint thus obtained being further strengthened on heating by the fused silicate attacking and combining with the adjacent fire-brick.

Water glass is also used in the preparation of artificial stone and fireproof materials, the principle being its reaction with soluble lime salts, with the production of gelatinous silica, which acts as a cementitious material, the alkali set free in the reaction being removed by washing and 'ageing.'

The stereochrome process of mural decoration employs water glass in a similar manner; a plaster surface is decorated by means of pigments mixed with water only, the colours being then fixed by spraying with water glass the alkali set free by its reaction with the lime in the plaster being carefully removed. Many other uses of this material depend on similar reactions.

Miscellaneous Uses of Glass.

Mosaic and tiles. By casting crude glass of various colours on to a slab and pressing it out by means of a roller or press, thick slabs or cakes are obtained, which can be cut up into small squares or 'tesseræ.'

Mosaic decoration is produced by arranging such squares according to a definite design and cementing them to a wall surface. By a modification of the same process the glass slab is moulded into the shape of tiles, and large slabs of variegated colours have been prepared for lining walls and making table tops in place of marble.

Another variety of vitreous mosaic or tile is prepared by heating a mixture of glass powder and sand until plastic and moulding it in a press. The waste mixture of sand and glass from plate-glass grinding can be employed for this purpose. The material has a peculiar semi-matt texture, and is opaque, owing to its containing half-vitrified sand in suspension.

Opus sectile is a similar material produced in thin sheets of various colours, which can be cut up by a diamond and painted with enamels to produce a wall decoration, which might be described as 'opaque stained glass.'

Glass bricks and paving stones have been introduced as a further development of this rough cast glass, but they offer no advantages over natural or artificial stone and ceramic ware.

Reaumur's porcelain, which was prepared on an industrial scale at one time, is made by heating various patterns of hollow ware to the softening-point until completely devitrified, the shape being preserved by embedding in sand during the process. An opaque porcelain-like material is thus produced, which, however, offers no particular advantages over genuine porcelain.

Artificial stone has been prepared by a modification of this process. Cullet and other waste glass is powdered, pressed into a mould and maintained at a red heat until it devitrifies.

Tempering. Attempts have been made to increase the mechanical strength of glass by cooling it quickly and uniformly; it is then, of course, in a condition of strain and stress, but these are uniformly distributed. A condition is attained similar to that of the well-known '*Rupert's drops*,' prepared by cooling drops of molten glass in water without allowing them to touch the walls of the containing vessel, when each drop assumes the form of a pear with a long thin tail. Their peculiarity is that the body of the drop is exceedingly hard, so hard, indeed, that it will stand a blow with a hammer without fracture, but as soon as a fragment of the tail is broken off the whole drop flies instantaneously into the minutest fragments. It was found by M. de la Bastie that glass vessels dropped into oil or melted mutton fat, which is kept at a temperature of 68°–75°C. (some authorities give 350°–400°C.), the glass being in a semi-ductile state, do not crack, but are rendered hard and difficult to break. The process has not become a commercial success, owing to the facts that the vessels sometimes go to pieces spontaneously after a year or more; that it is difficult to apply the process to wine decanters or water bottles, for the air cannot easily be expelled from the interior so as to allow it to share in the process of tempering; that the vessels are brittle, though they cannot perhaps be so easily broken as those which have not undergone the process; lastly, that such vessels cannot be ground or cut without flying to pieces.

Hardening. The Siemens process depends on the principle that glass, if evenly cooled, however quickly, is under little strain, and that the more rapidly it loses heat the harder its surface becomes. A sheet of glass, for example, loses heat more rapidly from its edges than from its surface, owing to the greater surface exposed. Hence it is under strain. But if the heat is rapidly and uniformly conveyed away from the surface, it retains its shape, and is hardened and not under strain. The cooling should be proportioned to the volume of the glass, not to its surface. The glass, which must be without flaw, is exposed suddenly and evenly to the radiant heat of a special furnace. The plate is then withdrawn and quickly placed between metal plates. The process of heating requires one minute, and the cooling half a minute. The sole of the heating furnace is smooth, and is covered with powdered talc to prevent the adhesion of the glass. The success of the process is due to the uniform temperature of the furnace, and to the fact that the heat is

wholly radiant. Owing to the extremely high temperature to which the plate is exposed, hard enamels may be used for ornamenting its surface. If required of extreme hardness, thin copper plates are applied to cool it. Iron plates give a less hard glass; and the effect may be reduced by covering the surface of the cooling plates with wire gauze, or by using asbestos paper or clay slabs. Bottles may also be hardened by heating them till soft, and then placing them in a case of iron in which they stand, prevented from touching the iron in more than three places by projecting ribs, or they may be heated in the casing, and then removed from the furnace and allowed to cool in the air. The most quickly cooled of such plates withstand eight times a shock which would break an ordinary plate, and those slowly cooled or semi-hardened, three times. They are not scratched by a diamond, and hence cannot be cut; but they may be polished, etched, and slightly ground if desired.

Reinforced glass. It is alleged that the mechanical fracture of windows may be prevented by cementing two sheets together by means of a sheet of transparent celluloid, softened at the surface by a solvent in order to produce optical continuity.

Bending. Both sheet and plate glass are bent into various curves for shop windows, street lamps, roof and deck lights, and various other purposes, by supporting the flat sheet on a bed of whitening shaped to the required curve by means of a template, and carefully heating to the softening-point in a reverberatory gas furnace, when the sheet gradually sinks by its own weight and takes the shape of the bed.

Cutting. 'Brilliant cutting' is performed by a series of operations similar to those employed in producing polished plate. A design is first cut into the glass by pressing against an iron wheel fed with sand, the rough surface thus produced being smoothed on similar wheels dressed with finer abrasive, and finally polished by a felt-covered wooden bobbin dressed with putty powder. The bevelling of plate-glass mirrors, &c., is performed by the same process.

At the present time glass cutting is largely used for the decoration of plate glass; it is also employed in the production of table ware and lustres, a soft flint glass being used, and the cutting so arranged as to take advantage of its high refraction to produce prismatic effect.

Engraving is performed in a similar manner to gem engraving, the glass being pressed against a small disc of soft iron revolved by means of a horizontal spindle in a small high-speed lathe. Glass cameos are produced by this method by engraving on a glass formed of two layers of different colours so as to cut away portions of the upper layer, leaving the design in relief on a background of the other colour.

Etching or embossing. Hydrofluoric acid is largely utilised in the decoration of hollow ware, and to a smaller extent in stained-glass work.

The portions of the glass to remain unacted upon are covered with a 'resist' (composed generally of a solution of bitumen and beeswax in turpentine) either by first coating the whole article and then scratching out the portions to be etched, or by applying the resist with a brush, or by means of a transfer.

The article is then immersed in the acid for a short time, washed and cleaned. If a weak solution of hydrofluoric acid is used, the etched portion is clear and transparent, but a matt surface is produced by 'white aciding,' in which a bath of acid sodium fluoride is used.

Thermometers and volumetric apparatus are graduated by this process, either by white aciding or by deeply etching with acid and filling in the lines with black japan, or preferably by burning in a soft vitreous enamel. The acid fluoride is also sometimes used in the laboratory for marking glass apparatus.

An extremely dilute solution of hydrofluoric acid forms an excellent means of cleaning glass vessels and apparatus, the shape of which renders ordinary cleaning difficult. The vessel filled with the solution is allowed to stand about 30 seconds, and immediately rinsed, the slight action on the surface is sufficient to loosen the attachment of impurities which float to the surface. The corrosion is, however, so slight that burettes may be cleaned by this method without impairing their accuracy. Photographic negatives can almost instantaneously be removed from their glass support by this method.

Sand blasting. The surface of glass may be readily abraded, leaving it rough and opaque, by impinging a stream of fine sand upon it by means of a powerful air blast. 'Ground glass' is produced in this manner, and any desired design may be produced by protecting portions of the surface by means of a metal stencil plate. Glass signs are produced in this way, either by cutting away the coloured surface of a flashed white glass, or by cutting deeply into white or opal glass, and filling in the cut portions with paint or vitreous enamel.

Drilling. The action of the sand blast just described is so powerful that large holes may be readily drilled in plate glass (such as in ventilators to shop windows) by its means. Small holes in spectacle glasses, instruments, &c., are drilled by means of a carbonado-pointed drill. 'Slitting,' or cutting glass into sections, is performed by means of a revolving soft-iron wheel fed with diamond-dust or carborundum.

Frosting or **'crystallising.'** Glass to be decorated by this means is first sand blasted, and then coated with a hot solution of hard glue, several coats being applied. It is then placed in a warm room, when the force exerted by the contraction of the glue, on drying, tears away the surface of the glass in a peculiar manner, giving it the appearance of a frosted window pane.

Stained or painted glass. In the production of stained-glass windows a special variety of sheet glass is used, which is made from imperfectly refined glass, and is irregular in colour, thickness, and texture. This is cut into shapes corresponding with the outlines of the design, the broad masses of colour being produced at the same time by selecting different colours for the various pieces. The details of the design and colouring are then produced on this background by painting each piece of glass with vitreous enamel.

The composition of this enamel determines the power of the window to withstand the severe conditions of exposure for an indefinite

period, and it has to fulfil several drastic conditions. It is prepared by first making a fusible and very complex glass, fairly rich in alkali, low in lime, and with a small percentage of lead, iron, and manganese, which is known as 'flux.' This is fused in a special furnace, arranged so that the molten glass can be run in a fine stream into cold water. The rough powder thus obtained is mixed with a compound of iron, manganese, and copper oxides prepared by precipitating the mixed carbonates from solution and igniting, and the whole subjected to a prolonged process of grinding, until it is reduced to an impalpable powder, which, when mixed with gum water, can be used in a brush after the manner of artists' colours.

The glass painted in this way is heated in a special furnace or 'kiln' to 'fire' the enamel on; gas furnaces are now almost universally employed for this purpose. The finished glass is then finally built up into the form of the window by joining the pieces of glass together by means of 'calms' of drawn lead having an H section.

The action of silver on glass (described above under *Colouring*) is largely utilised in the craft to produce local yellow colouration, technically known as 'silver stain.'

Photographic decoration. This is a modification of the last process, in which the design, instead of being painted by hand, is reproduced in the glass by a modification of the carbon process, the details of production being otherwise the same. This method of working is only suitable for designs of a mechanical nature, and is used for the production of advertisement tablets and so forth.

Iridescent glass. Beautiful effects are produced on glasses rich in silica by corrosion of the surface, the silica being left on the surface in a thin film, producing prismatic colours by interference. The specimens of iridescent Roman glass to be seen in all museums owe their beauty to the effect produced in this way by prolonged burial. This effect may be imitated by heating the manufactured article with water containing 15 p.c. of hydrochloric acid under pressure (Fremy and Clémandot); or, more easily, by exposing the glass while hot to the fumes of stannous chloride, by sprinkling a little of that salt on the ledge of the furnace while heating the vessel (Powell).

Glass vases, &c., rendered iridescent in this manner, are produced in large numbers at the present time, and a richly iridescent variety of sheet glass known as 'Luna' is also manufactured for special purposes.

Gilding. Glass is gilt by painting it with 'liquid gold,' which is chloride of gold dissolved in balsam of sulphur. The prepared glass is then fired at a gentle heat, when a film of metallic gold is deposited on the surface. Silver and platinum can also be deposited in this way. The film is exceedingly thin, but it may be increased to a considerable thickness by electroplating. Very richly ornamented glassware is produced in Bohemia by this latter method.

Glass mirrors. Various metals, mercury, copper, silver, gold, platinum, may be deposited on glass, converting it into a mirror. Usually mercury is used for the purpose. A flat surface is covered with tin foil, all creases and wrinkles being smoothed out with a soft brush. A little mercury is poured on the foil and spread over the whole surface with a woollen cloth. The table is surrounded with a beading, and mercury is poured in it until it reaches a depth of a fifth of an inch. A narrow strip of paper is then pushed in between the foil and the mercury resting on it; the edge of the glass plate, previously thoroughly cleaned, is then placed on the paper, and the plate, held in a nearly horizontal position, is then pushed along, the paper on which it rests slipping on the surface of the foil. When the plate rests on the mercury, the table is inclined by jack screws at one end, so that the mercury runs off, leaving the plate resting on the amalgamated foil. A woollen cover is then placed on the plate, and it is then weighted down, the weights being gradually increased. The table is gradually tilted, till after 24 hours it is inclined at an angle of 10° or 15°. The plate is then lifted and set on its edge in a trough into which the excess of mercury drains. After about 4 weeks all superfluous mercury has drained off and the mirror is finished.

The silvering of glass was introduced by Drayton in 1843. His process was subsequently modified by Liebig. The following solutions are employed: 1 part of fused silver nitrate dissolved in 10 parts of water; a solution of ammonium nitrate of 1·115 sp.gr., or of ammonium sulphate of 1·106 sp.gr.; a solution of caustic soda absolutely free from chlorine of 1·050 sp.gr. These three solutions are mixed in the proportions: 100 volumes of the ammonia solution, 140 volumes silver solution, and 750 volumes soda solution. The silver solution is poured into the ammonium sulphate, and the soda added in small quantities at a time. It is then allowed to settle for 3 days, and the clear portion siphoned off. 50 grams of white sugar candy are dissolved and boiled with 3·1 grams of tartaric acid for an hour, and then diluted to 500 c.c., 2·857 grams of copper tartrate are dissolved in water, caustic soda is added until the initial blue precipitate is redissolved, and the solution is then diluted to 500 c.c. One volume of the sugar solution and one volume of the copper solution are mixed, and eight volumes of water added. Immediately before use 50 volumes of the silvering solution are diluted with 250–300 volumes water at 28°–30° mixed with 10 volumes of the reducing solution, and poured into a shallow trough; the glass plate is then laid on this solution and left for some hours. The silver is precipitated on the surface of the glass. It is then washed, dried, and polished by gentle rubbing with chamois leather. The silver deposited on a square metre of glass weighs 3–3·5 grams. Numerous other recipes are also given, the chief difference being in the materials used for reduction.

Glass can also be platinised and gilt, but these processes are not carried out on a large scale. For a method of depositing copper on glass, *v.* HYDRAZINES. N. H.

GLASS OF ANTIMONY *v. Antimony crocus*, art. ANTIMONY.

GLASS, TOUGHENED, *v.* GLASS.

GLAUBER'S SALT. *Sodium sulphate* (*v.* SODIUM).

GLAUBERITE *v.* CALCIUM.

GLAZES *v.* FRITTS AND GLAZES; also POTTERY.

GLIADIN *v.* GLUTEN.

GLOBULINS *v.* PROTEINS.

GLUCINUM (*Beryllium*); Gl.; 9·1 (Parsons, J. Amer. Chem. Soc. 1905, 27, 1204), occurs in *beryl, euclase, phenacite, chrysoberyl, leucophane, helvite, davalite,* and other minerals. The element was detected by Vauquelin in 1798, but the metal was first isolated by Wöhler in 1828 by fusing the chloride with potassium. Glucinum can be prepared by the electrolysis of a fused mixture of the chloride with sodium or ammonium chloride (Borschers, Chem. Zentr. 1895, ii. 13), or of the fused double fluorides, GlF_2, NaF; or GlF_2, 2NaF (Lebeau, Compt. rend. 1898, 126, 744).

Glucinum may be prepared by electrolysing the minerals containing it between metallic electrodes in the presence of fluorine or one of its compounds, either alone or with the addition of a halogen compound of an alkali or alkaline earth (Liebmann, J. Soc. Chem. Ind. 1899, 282; Eng. Pat. 3497).

Warren (Chem. News, 1895, 72, 310) describes the following process :—

Pulverised and lixiviated beryl is fused for 3 hours in a blast furnace with four times its weight of sodium carbonate, after which the solidified mass is decomposed by superheated steam, and then by hydrochloric acid, evaporated to dryness and extracted with water. The solution is now freed from iron and chromium by the acetate method, and excess of sodium carbonate added; the precipitate is treated with excess of sulphurous acid, whereby the alumina and glucina pass into solution. On boiling, the alumina is precipitated, excess of ammonium carbonate is now added to the filtered solution, which is well boiled. The precipitate of glucinum carbonate thus obtained is ignited with lampblack out of contact with air, then submitted to the action of bromine at a red heat in clay retorts, when glucinum bromide distils over and is reduced electrolytically. It is also prepared by the reduction of the oxide with aluminium (Just and Mayer, J. Soc. Chem. Ind. 1909, 528; D. R. P. 208402).

Glucinum is a hard metal, with a bright silver-white colour, melting at about 1400°; sp.gr. 1·93; sp.ht. 0·4246. The powdered metal takes fire when heated in air, burning with great brilliancy, and dissolves readily in dilute acids, also in caustic alkalis, with evolution of hydrogen; but it does not decompose water even at a red heat. It is generally regarded as divalent (Combes, Compt. rend. 1894, 119, 1221; Henry, *ibid.* 1895, 121, 600; Retgers, Zeitsch. physikal. Chem. 1896, 20, 481; Galecki, Zeitsch. Elektrochem. 1908, 14, 767). Tanatar (J. Russ. Phys. Chem. Soc. 1904, 36, 82; 1906, 38, 850), from various organic derivatives, regards the metal as tetravalent.

Glucinum yields useful alloys with various metals by heating the oxides with carbon in the electric furnace, or by the electrolysis of a mixture of the fused metal with the double fluoride of glucinum and sodium in a carbon crucible as anode. The 5 p.c. alloy with copper is malleable, readily filed and polished, and unaffected by air; an alloy containing less glucinum is sonorous (Lebeau, Compt. rend. 1897, 125, 1172; 126, 744; Liebmann, D. R. P. 94507, 1896; Chem. Zentr. 1898, i. 484).

Compounds. *Glucinum oxide* or *glucina* GlO is obtained from beryl by heating the coarsely powdered mineral with 6 parts of ammonium hydrogen fluoride for 10–12 hours at a temperature not exceeding a dull red heat. The mass is then treated with water, and the insoluble aluminium fluoride removed by filtration. The filtrate is evaporated to dryness, and heated with strong sulphuric acid, thus removing fluorine and silica. The solution obtained on adding water is treated with nitric acid to oxidise iron, and the filtered liquid is poured into an excess of ammonium carbonate solution. Hot water is now added, after which the solution is filtered, mercuric chloride added, and the remaining iron is precipitated with ammonium sulphide. The filtered solution is boiled, whereupon basic glucinum carbonate is precipitated, which, on ignition, yields pure glucina (Gibson, Chem. Soc. Trans. 1893, 909; Lebeau, Compt. rend. 1895, 121, 641; Pollok, Chem. Soc. Trans. 1904, 603). Various other methods of preparing glucina from minerals have been described by Krüss and Moraht (Ber. 1890, 23, 727), and by Bran and Oordt (J. Soc. Chem. Ind. 1906, 1147; Eng. Pat. 15973, 1906).

It is a white amorphous powder of sp.gr. 3·016, which fuses in the electric arc, forming, after cooling, a crystalline mass, which is harder than ruby. In the electric furnace it is reduced by, and forms crystalline compounds with, boron, silicon, and carbon (Lebeau, Compt. rend. 1896, 123, 818).

The oxide acts as a feeble acid towards strong bases, forming the salts $Gl(OK)_2$, whilst with feeble acids it acts as a base, yielding such salts as $(GlSO_3)_x$·GlO (Krüss and Moraht, *l.c.*; Seubert and Elten, Zeitsch. anorg. Chem. 4, 44). It is insoluble in water, but dissolves in strong sulphuric acid, yielding the sulphate, and also in fused potassium fluoride (Duboin, Compt. rend. 1896, 123, 698). According to Winkler (Ber. 1891, 24, 1966), when the oxide is heated with magnesium at red heat in a current of hydrogen, *glucinum hydride*, having an unpleasant smell and slowly decomposed by warm water, is formed.

Glucinum hydroxide $Gl(OH)_2$ is formed by precipitating glucinum salts with ammonia, and can be separated from aluminium and iron by digestion with glacial acetic acid, when it is converted into a basic glucinum acetate, which is readily soluble in chloroform (Haber and Oordt, Zeitsch. anorg. Chem. 1904, 40, 465; D. R. P. 155466; Oordt, J. Soc. Chem. Ind. 1904, 799).

Glucinum hydroxide, when freshly precipitated, is gelatinous, readily absorbs carbon dioxide, and is soluble in dilute acids, alkalis, and alkali carbonates. On being heated with water, alkali carbonates, or ammonia, or when allowed to stand for some time at the ordinary temperature, it loses the above-described properties (Haber and Oordt, Zeitsch. anorg. Chem. 1904, 38, 377; D. R. P. 165488). Unlike aluminium hydroxide, glucinum hydroxide is quite insoluble in ammonia, or in methyl- or ethylamine (Renz, Ber. 1903, 36, 2751).

Glucinum chloride $GlCl_2$ is formed by passing a current of dry chlorine over a mixture of the

oxide and sugar charcoal, heated to bright redness in a porcelain tube (Pollok, Chem. Soc. Trans. 1904, 604). It forms white needle-shaped crystals, melting at 400°, and boiling at about 500°. It forms a hydrated chloride $GlCl_2,4H_2O$, and also double salts with platinum, tin, and mercuric chloride, and with iodine trichloride (Weinland and Schlegelmilch, Zeitsch. anorg. Chem. 1902, 30, 134).

Glucinum iodide GlI_2 is obtained by heating the carbide in a stream of hydriodic acid, carrying iodine vapour; it melts at 510°, combines with ammonia to form $2GlI_2,3NH_3$; and yields crystalline compounds with aniline, pyridine, and other organic bases. With bromine it yields the corresponding bromide (Lebeau, Compt. rend. 1898, 126, 1272). It forms a double salt with lead iodide (Mosnier, Ann. Chim. Phys. 1897, 12, [vii.] 374).

Glucinum fluoride is obtained by the action of hydrofluoric acid on the oxide. It is soluble in water and alcohol, melts at 800°, and is converted by oxygen into the oxyfluoride $5GlF_2,2GlO$ (Lebeau, *l.c.*; and 1418).

Glucinum carbonates. Basic carbonates are formed when a glucinum salt is treated with an alkali carbonate. If carbon dioxide be passed through the aqueous solution or suspension of the basic carbonate, and the solution then evaporated in an atmosphere of carbon dioxide, the normal salt $GlCO_3,4H_2O$ separates.

Glucinum sulphates. The following sulphates have been obtained: $GlSO_4,6H_2O$; $GlSO_4,4H_2O$; $GlSO_4,2H_2O$; $GlSO_4,H_2O$; $GlSO_4$ (Parsons, J. Amer. Chem. Soc. 1904, 26, 1433; Leri Malvano, Zeitsch. anorg. Chem. 1906, 48, 446). Also the *thiosulphate* $GlS_2O_3,11H_2O$ (Faktor, Chem. Zentr. 1901, ii. 878); and *sulphites* (Seubert and Elten, Zeitsch. anorg. Chem. 4, 44).

Glucinum chromate $GlCrO_4,H_2O$ has been obtained by evaporating a solution of the carbonate in concentrated chromic acid. It forms reddish-yellow crystals, which are decomposed by water, forming the basic salt $GlCrO_4,6Gl(OH)_2$, which can also be obtained by precipitating glucinum sulphate with ammonium chromate (Glassmann, Ber. 1907, 40, 2402).

Glucinum carbide GlC_2 is obtained by heating the oxide with carbon in the electric furnace (Henry, Compt. rend. 1895, 121, 600; Lebeau, *ibid.* 496). It forms microscopic yellowish-brown crystals, which scratch quartz, and are decomposed by water with formation of pure methane. Also decomposed by hot concentrated alkalis, and by halogen acids, yielding the corresponding halide.

Glucinum borocarbide $C_4B_6Gl_6$, obtained when glucina is heated with boron in a carbon boat in the electric furnace, forms brilliant crystals with a metallic lustre; sp.gr. 2·4, readily soluble in acids, and not decomposed by water (Lebeau, Compt. rend. 1898, 126, 1347).

Glucinum phosphates (Rammelsberg, Chem. Zentr. 1891, ii. 790; Sestini, Gazz. chim. ital. 20, 313; Ouvrard, Compt. rend. 1890, 110, 1333), *tungstates* and *silico-tungstates* (Tanatar and Kurowski, J. Russ. Phys. Chem. Soc. 1909, 41, 813; Wyrouboff, Bull. Soc. Franc. Min. 1896, 19, 240), *molybdates* (Rosenheim and Wose, Zeitsch. anorg. Chem. 1897, 15, 283, 306, 307), and *columbates* (Larsson, *ibid.* 1896, 12, 188) have been obtained. Organic acids react with glucinum carbonate, forming salts of the type Gl_4OX_6, $Gl_4OX_2X'_4$, and $Gl_4OX_3X'_3$ (X, X' being organic radicles) (Tanatar and Kurowski (J. Russ. Phys. Chem. Soc. 1907, 39, 936; Lacombe, Compt. rend. 1902, 134, 772; Glassmann, Ber. 1908, 41. 33; Parsons and Sargent, J. Amer. Chem. Soc. 1909, 31, 1203).

Other organic compounds of glucinum are described by Wyrouboff (*l.c.*); Kurowski (J. Russ. Phys. Chem. Soc. 1907, 39, 1630; 1908, 40, 580, 787); Curtius and Rissom (J. pr. Chem. 1898, [ii.] 58, 261); Glassmann (Ber. 1907, 40, 3059; Chem. Zeit. 1907, 31, 8).

GLUCONASTURTIIN, GLUCOTROPÆOLIN *v.* GLUCOSIDES.

GLUCOSAMINE *v.* CARBOHYDRATES.

GLUCOSE *v.* CARBOHYDRATES.

GLUCOSIDES. The glucosides are a large and important group of substances occurring almost exclusively in the vegetable kingdom, which, by the operation of hydrolysis, involving the addition of the elements of water, are resolved into sugar and another compound not belonging to the class of carbohydrates. The sugar thus formed is usually glucose or rhamnose; certain glucosides yield other carbohydrates, some of which have not yet been identified.

The hydrolysis may often, but not always, be rapidly effected by heating with dilute acids. It may also be brought about by the action of appropriate enzymes, such as emulsin, myrosin, &c.

Glucosides are, in many cases, far more resistant to hydrolysis by acids than is generally supposed, and almost invariably their behaviour towards acids is in marked contrast to the ease with which they are hydrolysed by the appropriate enzyme. There is some evidence that the nature of the acid is not without influence, some glucosides being more easily hydrolysed by hydrochloric than by sulphuric acid.

As a rule, a plant containing a glucoside also contains a corresponding enzyme capable of hydrolysing it, the enzyme being present also in allied species which do not contain the glucoside. On the other hand, the elder (*Sambucus nigra*, Linn.) affords an example of a plant containing a glucoside, accompanied by very little of the corresponding enzyme. Enzyme and glucoside do not exist in the same cell, but they are brought together should the cellular structure be damaged or rendered permeable.

In the greater number of cases only one variety of sugar is formed on hydrolysing a glucoside, although, in some instances, two different carbohydrates are produced, or possibly two or more glucose molecules; in such cases the simple sugar molecules are probably united as di- or tri-saccharides. Using appropriate enzymes or acids of different degrees of concentration, it is possible to remove the sugar groups one at a time, and so form new glucosides. Thus, from amygdalin, by the action of the enzyme amygdalase, which is present in some varieties of yeast, the glucoside of mandelonitrile is formed together with glucose.

The majority of the glucosides are colourless, crystalline neutral compounds, one or two are basic, and a few are acidic. They are usually soluble in water and alcohol, and but very sparingly soluble in ether. They crystallise

with one or more molecules of water, which is lost on heating. They are charred when heated to a moderately high temperature, occasionally a sublimate of the non-sugar component being obtained. They are not acted upon by Fehling's solution, so far as the sugar part of the molecule is concerned. Many of them are optically active, and, as a rule, rotate rays of polarised light to the left, although derived from a dextro-rotatory carbohydrate. They have often a bitter taste, and a therapeutic action, being the active principle of many plant extracts used in pharmacy. The general behaviour of the glucosides and their close relationship to the synthetic methyl glucosides (*v.* CARBOHYDRATES) establishes their structure beyond doubt as:

$$R{\cdot}O{\cdot}CH{\cdot}(CH{\cdot}OH)_2{\cdot}CH{\cdot}CH(OH){\cdot}CH_2(OH).$$
$$\qquad\qquad\quad O$$

In many instances the radicle R is a poly-hydroxy- compound, and it is not in all cases certain to which of the hydroxyl groups the sugar residue is attached.

It is further of interest that no natural glucoside has been found in two stereoisomeric forms corresponding to the α- and β-methyl glucosides. Judging from their behaviour towards the emulsin of almonds, many of the natural compounds are considered to be derived from *β-glucose*. This view has been confirmed in some instances by the fact that glucose is first separated as the β- form of low rotatory power on hydrolysing the glucoside, and afterwards undergoes isomeric change to the equilibrated mixture of α- and β-glucose. In fact, no glucosidic derivative of α-glucose has yet been described as occurring naturally.

In addition to a few of the natural glucosides of plants, other glucosides have been prepared in the laboratory. The isomeric α- and β-methyl glucosides are discussed under CARBOHYDRATES; glucosides of primary alcohols, *e.g.* ethyl, glycerol, and benzyl glucosides, are obtained by the same method by the interaction of glucose and alcohol in presence of hydrogen chloride.

An alternative method first used by Colley involves the interaction of tetraacetylchloro-glucose $C_6H_7OCl(OAc)_4$, and the sodium derivative of alcohols or phenols. Sodium chloride and the tetraacetate of the desired glucoside are formed, and the latter is subsequently hydrolysed to eliminate the acetyl groups. In this way the natural compounds, helicin, methylarbutin, and a number of new glucosides, including those of the terpenes and of some thiophenols, have been prepared.

The function of glucosides has been a subject of considerable discussion. They have been regarded as reserve materials; as antiseptics, and, therefore, bactericidal in character; and as protectives, on the assumption that the bitter taste and poisonous properties of many would act as a warning to animals. A more recent view is that the non-sugar constituents function as hormones; that is, they are able to penetrate the plant cells and stimulate the protoplasm to greater activity; much evidence has been adduced in favour of this view (*see* E. F. Armstrong, The Simple Carbohydrates and Glucosides, London, Longmans, 1910).

Preparation.—Glucosides are obtained from plants by extraction with water or alcohol, the abstract being subsequently purified in a variety of ways to eliminate other soluble substances. The extraction of the plant material is often conveniently performed in a Soxhlet apparatus; and ethyl acetate will sometimes be found to be a convenient solvent. It is essential in most cases to destroy the accompanying enzyme before extracting with water, so that hydrolysis may not take place.

For convenience of reference only the most important glucosides are here described in alphabetical order. They are, perhaps, better classified in groups according to the nature of the non-sugar constituent, and brief reference may therefore be made to these groupings. Special works dealing with the glucosides are: *Van Rijn*, Die Glucoside, Berlin, 1900; *Roscoe-Schorlemmer's Chemie*, Band 8, Pflanzen Glucoside, Braunschweig, 1901; *Armstrong*, The Simple Carbohydrates and Glucosides, London, 1910, in all of which numerous references to the original literature will be found.

Phenols occur very frequently as constituents of glucosides, especially those containing two and more hydroxyl groups. The sugar residue is attached to a phenolic hydroxyl rather than to an aliphatic alcohol group in a side chain, *e.g.* salicin, coniferin.

Aldehydes. A number of glucosides of benzaldehyde exist, but in most of these hydrogen cyanide is attached to the aldehyde group. The relationship of amygdalin, and the three amygdonitrile glucosides, *prulaurasin*, *sambunigrin*, and *prunasin*, is of considerable interest. *Salinigrin*, the glucoside of *m*-hydroxybenzaldehyde, is isomeric with *helicin*, the glucoside of *o*-hydroxybenzaldehyde, obtained by oxidising salicin, but not yet found in plants. *Dhurrin* is a derivative of *p*-hydroxybenzaldehyde.

Acids. Glucosides of the higher fatty acids are characteristic of the *convolvulaceæ*, and are used as purgatives.

Coumarins. The glucosides of the coumarin group are interesting. That of coumarin itself has not yet been isolated, though there can be little doubt that coumarin, which is so widely distributed in plants, is present in this form. Skimmin is a monohydroxycoumarin; æsculin and daphnin are isomeric dihydroxycoumarins; fraxin, a trihydroxycoumarin. Scopolin is the methyl ether of æsculin.

Hydroxyanthraquinone glucosides are madder, frangulin, and others, like aloes, which form emodin on hydrolysis.

Hydroxyflavone glucosides all give yellow dyestuffs. Those described are apiin, fustin, gossypitrin, incarnitrin, quercimeritrin, quercitrin, *iso*quercitrin, robinin, rutin, serotin, vixetin, xanthorhamnin. They are mostly rhamnosides.

The following glucosides contain rhamnose: *Baptisin, convallamarin, datiscin, frangulin, fustin, glycyphyllin, hesperidin, kampheritrin, ouabain, naringin, quercitrin, robinin, rutin, solanin, strophantin, trifolin, α-turpethein, xantho-rhamnin.*

Those containing pentoses other than rhamnose are: *Aloin, antiarin, convolvulin, gentiin, jesterin, quinovin, saponin, β-turpethein, vicianin.*

The following contain galactose: *Convallamarin, digitonin, robinin, sapotoxin, solanin.* Lævulose has so far only been obtained from

alliin, the glucoside of garlic (Rindquist, Apoth. Zeit. 1910, 25, 105).

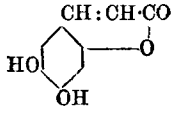
The glucosides hydrolysed by emulsin are: *Æsculin, amygdalin, amygdonitrile glucoside, androsin, arbutin, aucubin, bankankosin, calmatambin, coniferin, daphnin, dhurrin, gentiopicrin, incarnatrin, indican, meliatin, oleuropein, picein, prulaurasin, salicin, sambunigrin, syringin, taxicatin, verbenalin.*

Adonin $C_{24}H_{40}O_9$, from *Adonis amurensis* (Reg and Rada) (*v.* Tahara, Ber. 24, 2579).

Æsculin $C_{15}H_{16}O_9$,2Aq, m.p. 205°, is found in the bark of the horse chestnut (*Æsculus hippocastanum*, Linn.), and in the roots of the wild jasmin (*Gelsemium sempervirens*, Ait.). It is very sparingly soluble in cold water, and crystallises in lustrous colourless prisms. Characteristic is the blue fluorescence of the aqueous solution, even when very greatly diluted; it is evident in a solution of 1 part of æsculin in 15 million parts of water. Alkali increases the fluorescence, acids destroy it. The aqueous solution is faintly acid. It gives a yellow solution with nitric acid, which, on the addition of ammonia, acquires a deep blood-red colour (comp. Schunck and Marchlewski, Annalen, 1894, 278, 353; Gattermann and Köbner, Ber. 1899, 32, 288). By the action of warm dilute mineral acids or of emulsin at 30°, æsculin is hydrolysed to glucose+æsculetin (a dihydroxycoumarin)

$$C_{15}H_{16}O_9+H_2O=C_6H_{12}O_6+C_9H_6O_4.$$

Æsculetin has the formula:



Æsculin is isomeric with daphnin.

Aloin, Barbaloin. The glucosides from the various species of aloe are but indefinitely characterised. They are decomposed into aloe emodin, which is a trihydroxymethyl anthraquinone identical with that derived from frangulin, and a sugar which is sometimes dextrose, sometimes a pentose. Léger (Bull. Soc. chim. 1910, 7, 479; and Compt. rend. 1910, 150, 1695) ascribes to barbaloin the formula $C_{20}H_{18}O_9$, and obtained from it on hydrolysis,, emodin and *d*-arabinose. Since the arabinose, which is a constituent of gums, &c., is *l*-arabinose, the occurrence of the *d*-isomeride is remarkable, as showing that sugars of both *d*- and *l*- series occur naturally.

Amygdalin $C_{20}H_{27}O_{11}N$,3Aq, m.p. 200°, $[\alpha]_D^{28}-38{\cdot}3°$, is the oldest known glucoside; it was first found by Robiquet and Boutron in 1830 in bitter almonds. The composition and mode of decomposition by emulsin into glucose, oil of bitter almonds, and hydrogen cyanide, was first indicated by Wöhler and Liebig. Besides the bitter almond, it is contained in the kernels of peaches, cherries, plums, apples, and in the fruits of most of the *Rosaceæ*. It crystallises from water in transparent rhombic prisms, from alcohol in glistening platelets. It is soluble in water, sparingly soluble in cold alcohol.

It is very readily hydrolysed by the emulsin of almonds to glucose (2 mols.), hydrogen cyanide, and benzaldehyde

$$C_{20}H_{27}O_{11}N+2H_2O=C_7H_6O+HCN+2C_6H_{12}O_6$$

Yeast contains an enzyme amygdalase, which hydrolyses it to glucose and amygdonitrile glucoside (*prunasin*)

$$C_{20}H_{27}O_{11}N+H_2O=C_6H_{12}O_6+C_{14}H_{17}O_6N,$$

which has since been found to occur naturally, and is, in its turn, hydrolysed by emulsin. Almond emulsin has been shown to be a mixture of three enzymes, which act consecutively.

Amygdalase first splits off one molecule of glucose, a *β-glucase* hydrolyses the amygdonitrile glucoside to β-glucose and *d*-mandelonitrile, and *cyanase* hydrolyses this last to benzaldehyde and hydrogen cyanide. It has not been possible to obtain the two glucose molecules from amygdalin united in the form of a disaccharide by means of plant enzymes, but using the digestive juices of the snail *Helix pomatia*, Giaja (Compt. rend. 1910, 150, 593) has demonstrated that a non-reducing disaccharide of the trehalose type is first formed, though subsequently hydrolysed to glucose. The disaccharide of amygdalin is definitely not maltose. Dilute acids act as almond emulsin does; strong hydrochloric acid hydrolyses amygdalin to *l*-mandelic acid, glucose, and ammonia. Concentrated sulphuric acid gives glucose and *d*-mandelonitrile.

On treatment with baryta, the *d*-mandelonitrile group in amygdalin is racemised and *iso*amygdalin is obtained. This is hydrolysed by amygdalase to prulaurasin. (For bibliography, *see* E. F. Armstrong, The Simple Carbohydrates and Glucosides; also Walker and Krieble, Chem. Soc. Trans. 1909, 95, 1437.)

Amygdonitrile glucoside (*Prunasin*)

$C_{14}H_{17}O_6N$,

m.p. 147°, $[\alpha]_D$ −26°, occurs in the young branches of *Prunus* (*Cerasus*) *Padus* (Linn.) (Hérissey, Arch. Pharm. 1907, 245, 641), and in the bark of the wild cherry, *Prunus serotina* (Ehrh.) (Power and Moore, Chem. Soc. Trans. 1909, 95, 243). It is obtained from amygdalin by the action of an extract of dried yeast (Fischer, Ber. 1895, 28, 1508). This enzyme amygdalase is only present in some specimens of brewers' yeast (top fermentation). Amygdonitrile glucoside is the β-glucose ether of *d*-mandelonitrile, *i.e.* the nitrile of *l*-mandelic acid (*cf.* prulaurasin and sambunigrin).

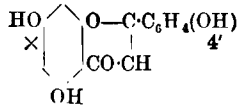
Androsin $C_{15}H_{20}O_8$,2Aq, m.p. 218°–220°, found in the rhizome of *Apocynum androsæmifolium* (Linn.) (Moore, Chem. Soc. Trans. 1909, 95, 734), forms long colourless needles, sparingly soluble in cold water or alcohol, readily in hot water. On hydrolysis by emulsin or sulphuric acid, it yields glucose and acetovanillone

$CH_3{\cdot}CO{\cdot}C_6H_3(OMe)(OH)$.

Antiarin. The latex of *Antiaris toxicaria* (Lesch.), an arrow poison, contains two glucosides. α-Antiarin $C_{27}H_{42}O_{10}$,4Aq crystallises in leaflets or plates; m.p. 220°–225°; it is hydrolysed to antiarose, *i.e.* a methyl pentose, and antiarigenin $C_{21}H_{30}O_5$. β-Antiarin $C_{27}H_{38}O_{10}$,3Aq or $C_{28}H_{38}O_{10}$,3Aq, crystallises in slender needles; m.p. 206°–207°. Emulsin has no action on either glucoside; both are toxic, their action resembling strophantin (Kiliani, Ber. 1910, 43, 3574).

Apiin $C_{26}H_{28}O_{14}$ (?), m.p. 228°, found in the leaves and seeds of parsley [*Carum* (*Apium*) *Petroselinum* (Bentl. and Hook.)], in celery [*A. graveolens* (Linn.)], and other umbelliferous plants; crystallises in small colourless needles;

sparingly soluble in cold, easily soluble in hot water and alcohol. The solutions readily gelatinise; they are strongly dextro-rotatory. It is hydrolysed by mineral acids with difficulty to glucose, apiose, a C_5 sugar with a branched chain of carbons (*v.* CARBOHYDRATES), and apigenin $C_{15}H_{10}O_5$, a hydroxyflavone derivative of the constitution



The sugar residue is probably united to the hydroxyl- group marked × (*see* Perkin, Chem. Soc. Trans. 1897, 71, 817).

Arbutin $C_{12}H_{16}O_7$,1Aq, m.p. 142°, and again at 194°, $[\alpha]_D$ −63·5°, occurs in the leaves of the bearberry [*Arctostaphylos Uva-ursi* (Spreng)], in a number of *Ericaceæ*, and in the leaves of the pear (Bourquelot, Compt. rend. 1910, 151, 81). Excepting in the pear, it is found associated with methyl arbutin, from which it cannot be separated by crystallisation. Hérissey effects this by the addition of potassium hydroxide to crude arbutin dissolved in alcohol. The syrupy precipitate is heated with acetic acid in alcohol, calcium carbonate added when it is in solution, the alcohol distilled off, and the residue extracted with water (Bull. Soc. chim. 1910, 7, 1054). Arbutin crystallises in long silky needles, gives a blue colouration with ferric chloride, and a sapphire-blue colour with Jungmann's reagent. It is hydrolysed by emulsin or by mineral acids to glucose and quinol; owing to the presence in emulsin of a small amount of oxydase, the quinol formed in this way becomes slightly oxidised, and the solution assumes a yellowish- or reddish-brown colour (*see* Bourquelot and Hérissey, Compt. rend. 1908, 146, 764; Bourquelot and Fichtenholz, J. Pharm. Chim. 1910, [vii.] 1, 62, 104; Hérissey, Compt. rend. 1910, 151, 444).

Methyl arbutin $C_{13}H_{18}O_7$,1Aq, m.p. 175°, $[\alpha]_D$ −64°; crystallises in needles; it gives no colouration with either ferric chloride or Jungmann's reagent. It is hydrolysed by emulsin more quickly than arbutin, yielding glucose and quinolmethyl ether (Hlasiwetz and Habermann, Annalen, 1875, 177, 334). It does not darken in colour on hydrolysis in presence of an oxydase. Methyl arbutin was synthesised by Michael by the interaction of acetochloroglucose with potassium quinol methyl ether (Amer. Chem. J. 1885, 6, 336).

Aucubin $C_{13}H_{19}O_8$,1Aq, m.p. 181° $[\alpha]_D$ −174°, is found in the seed, leaves, stem, and roots of the Japanese variegated laurel, *Aucuba japonica* (Thunb.) and allied species. It is hydrolysed by mineral acids and by emulsin to glucose and aucubigenin ($C_7H_9O_3$). The latter has not been isolated; it is condensed to an intense black-coloured product immediately it is formed. It is this compound which causes *aucuba* leaves to become black when put in an atmosphere of chloroform for a few minutes. (Literature summarised by Bourquelot and Hérissey, Ann. Chim. Phys. 1905, [viii.] 4, 289.)

Baptisin $C_{28}H_{32}O_{14}$,9Aq, m.p. 240°, $[\alpha]_D$ −61°, found in the roots of *Baptisia tinctoria* (R.Br.), crystallises in reniform aggregates of slender needles, sparingly soluble in water; it is hydrolysed to rhamnose (2 mols.) and baptigenin $C_{14}H_{12}O_6$, a phenol containing three hydroxyl groups (Gorter, Arch. Pharm. 1897, 235, 303). *ψ-Baptisin* $C_{27}H_{30}O_{14}$,4Aq, m.p. 247°, which occurs in the same root is hydrolysed to glucose, rhamnose, and *ψ*-baptigenin $C_{15}H_{10}O_5$ or $C_{12}H_6\langle^{O\cdot CH:CH\cdot OH}_{O\cdot CHO}\rangle O$ (Gorter, Arch. Pharm. 1907, 245, 561).

Calmatambin $C_{19}H_{28}O_{13}$,2Aq, m.p. 144°, $[\alpha]_D$ −130°, found in the bark of *Canthium glabriflorum* (Hiern.) from Sierra Leone, crystallises in colourless prismatic needles. It is hydrolysed by mineral acids and by emulsin to glucose and *Calmatambetin* $CH_3O\cdot C_{12}H_{10}O_2(OH)_5$. It is physiologically inactive (Pyman, Chem. Soc. Trans. 1907, 91, 1228).

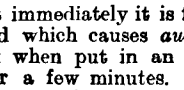
Coniferin $C_{16}H_{22}O_8$,2Aq, m.p. 185°, $[\alpha]_D$ −67°, was discovered in the cambial sap of *Larix decidua* (Mill.), and occurs in the saps of the conifers in general; it is found also in beetroot and asparagus.

It crystallises in colourless rosettes of pointed needles, sparingly soluble in cold water. The aqueous solution has a slightly bitter taste. When moistened with phenol and concentrated hydrochloric acid, an intense blue colour is formed; it is soluble in concentrated sulphuric acid with a red colouration. It is decomposed by heating with mineral acids, but emulsin hydrolyses it to glucose and coniferyl alcohol $C_6H_3(OH)(OMe)C_3H_4\cdot OH$.

On oxidation with permanganate, glucovanillinic acid $C_6H_3(OMe)(CO_2H)OC_6H_{11}O_5$ is obtained, m.p. 211°. Chromic acid oxidises coniferin to glucovanillin, m.p. 192°, which is hydrolysed by emulsin or by acids to glucose and vanillin (*see* Tiemann and Haarmann, Ber. 1874, 7, 608; 1875, 8, 509, 1127; 1876, 9, 408, 1278).

Convolvulin $C_{54}H_{96}O_{27}$, m.p. 150°, is found in jalap root, *Ipomœa purga* (Hayne). It is a colourless amorphous powder, very sparingly soluble in water, but readily soluble in alcohol and acetic acid, and dissolves in concentrated sulphuric acid with a red colouration. It is hydrolysed by acids to dextrose, rhodeose, and convolvulinolic acid $C_{15}H_{30}O_3$. This acid, on oxidation, takes up 2 molecules of oxygen, forming methylethyl acetic acid and ipomic acid $C_{10}H_{18}O_4$, an isomeride of sebacic acid (*cf.* Votoček, Ber. 1910, 43, 476).

Daphnin $C_{15}H_{16}O_9$,2Aq, m.p. 200°, is a constituent of the bark of *Daphne mezereum* (Linn.) and *D. alpina* (Linn.). It forms long colourless needles or prisms, sparingly soluble in water, easily soluble in alcohol. It is faintly acid, and has a bitter astringent taste. It is soluble in alkalis and their carbonates with a golden-yellow colour, the solutions decompose on boiling. On hydrolysis by acids or by emulsin, glucose and daphnetin



are formed (comp. Stünkel, Ber. 1879, 12, 109).

Datiscin $C_{21}H_{24}O_{11}$,2Aq, m.p. 190°, present in the leaf and roots of *Datisca cannabina* (Linn.),

forms colourless lustrous needles. On hydrolysis by acids rhamnose and datiscetin

$$C_6H_4\langle\begin{matrix}CO\\O\end{matrix}\rangle C_6(OH)_2(OMe)_2$$

are formed (Schunck and Marchlewski, Annalen, 1893, 277, 261; 1894, 278, 351).

Dhurrin $C_{14}H_{17}O_7N$ was obtained from the great millet, *Sorghum vulgare* (Pers.), by Dunstan and Henry (Phil. Trans. 1902, A, 199, 399). It is hydrolysed by emulsin and by dilute hydrochloric acid to glucose, hydrogen cyanide, and *p*-hydroxybenzaldehyde. It is the glucoside of *p*-hydroxymandelonitrile.

Digitalis glucosides. The leaves and seed of the foxglove, *Digitalis purpurea* (Linn.), contain glucosides, which increase the activity of all forms of muscle tissue, more especially that of the heart and arterioles. The leaves contain digitalin, digitoxin, and, perhaps, digitalein, the existence of this as an entity being uncertain. The seeds contain digitalin and digitonin, a glucoside of the saponin class, which is possibly also present in the leaves (*v.* DIGITALIS).

Digitalin $C_{35}H_{56}O_{14}$ or $C_{36}H_{58}O_{14}$, m.p. 217°, is obtained from commercial German digitalin by extraction with ether-alcohol. It occurs in characteristic colourless granular masses, and crystallises in needles from 85 p.c. methyl alcohol. It is very sparingly soluble in cold water, readily in alcohol. Concentrated sulphuric acid dissolves it with a golden-yellow colouration, which changes to a magnificent rose-red or violet-red on the addition of potassium hypobromite. Sulphuric acid containing a little ferric oxide gives, with digitalin, at first an intense golden-yellow, and then a red colour changing to a permanent reddish-violet.

It is hydrolysed on heating with dilute alcoholic hydrogen chloride to glucose, a sugar $C_7H_{14}O_5$ named digitalose, and digitaligenin $C_{22}H_{30}O_3$ or $C_{23}H_{32}O_3$, which last crystallises in granular aggregates of needles; m.p. 210°. Digitalin possesses the characteristic action on the heart without being cumulative.

Digitonin $C_{54}H_{92}O_{28}$ or $C_{55}H_{94}O_{28}$, m.p. 225°, $[\alpha]_D -50°$, forms one-half of the mixed glucosides from digitalis seed, and the principal proportion of commercial German digitalin. To obtain it the commercial product is dissolved in 85 p.c. alcohol at 50°–60°, and allowed to crystallise slowly; digitonin then separates. When pure it crystallises in crusts of slender needles, very sparingly soluble in water, readily soluble in alcohol. The hot aqueous solution is opalescent, and the glucoside does not separate on cooling. The aqueous solution froths like that of saponin. It gives a red colouration with concentrated sulphuric acid, and, on heating with concentrated hydrochloric acid, becomes yellow, then red, and finally somewhat blue. It is hydrolysed on heating with alcoholic hydrogen chloride to glucose (2 mols.), galactose (2 mols.), and digitogenin $C_{30}H_{48}O_6$ or $C_{31}H_{50}O_6$, crystallising in slender needles, which soften at 250°. Digitonin is poisonous, but does not possess the action on the heart peculiar to digitalis. It forms crystalline compounds with amyl alcohol and other alcohols, and with phenol, and combines with 1 mol. cholesterol in alcoholic solution to give a crystalline precipitate, which is no longer poisonous. This is a valuable test for digitonin.

Digitoxin $C_{34}H_{54}O_{11}$, the most active principle of digitalis leaves, is cumulative in its action; it is the chief constituent of 'Nativelle's crystallised digitalin,' or 'French digitalin.' It is obtained by extracting the leaves with water, and then with alcohol, precipitating the alcoholic solution with lead acetate, evaporating and extracting the residue with chloroform. It crystallises from chloroform in thin anhydrous prisms, which are not melted at 240°, and from dilute alcohol in hydrated crystals; m.p. 145°. It is insoluble in hot or cold water, soluble in alcohol, chloroform, or ether. When it is dissolved in glacial acetic acid, a drop of ferric chloride added, and then concentrated sulphuric acid is cautiously poured down so as to form a layer under the acetic acid, a dirty brownish-green band appears, which alters to a broad intense bluish-green band at the dividing zone. It is hydrolysed by alcoholic hydrogen chloride at the ordinary temperature to digitoxigenin $C_{23}H_{32}O_4$, colourless crystals, m.p. 230°, and 2 molecules digitoxose $C_6H_{12}O_4$, a sugar having the constitution:

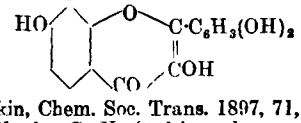
$$CH_3\cdot CH(OH)\cdot CH(OH)\cdot CH(OH)\cdot CH_2\cdot CHO.$$

It crystallises in prisms, m.p. 102°, and is dextro-rotatory.

Frangulin $C_{21}H_{20}O_9$, m.p. 228°, found in the bark, root bark, seeds, and fruit of the berry-bearing alder, *Rhamnus frangula* (Linn.), and also in *R. carthartica* (Linn.), is a yellow silky glistening microcrystalline powder, nearly insoluble in water, readily soluble in alcohol and benzene. It dissolves in alkalis with an intense cherry-red colour. It is hydrolysed by acids to rhamnose and emodin (trihydroxymethylanthraquinone) (comp. Schwabe, Arch. Pharm. 1888, 226, 569; Thorpe and Miller, Chem. Soc. Trans. 1892, 61, 1).

Fraxin $C_{16}H_{18}O_{10}$, m.p. 320°, obtained from the bark of the ash *Fraxinus excelsior* (Linn.), and from several *Æsculus* and *Pavia* species, crystallises in colourless needles, sparingly soluble in cold water, but easily in hot water and alcohol. The solutions, like those of æsculin fluoresce blue. It is hydrolysed by dilute sulphuric acid to glucose and fraxetin $C_{10}H_8O_5$, the monomethyl ether of a trihydroxycoumarin. It contains a methoxyl group more than daphnin or æsculin (*see* Rochleder, Wien. Akad. Ber. 1863, 48, 236).

Fustin $C_{30}H_{26}O_{14}$, m.p. 218°, the glucoside of fustic (*Rhus cotinus* [Linn.]), forms small needles of silvery lustre. Dilute sulphuric acid hydrolyses it to rhamnose and 2 molecules of fisetin $C_{15}H_{10}O_6$, which is a 3:3':4'-trihydroxyflavonol of the following constitution:



(*see* Perkin, Chem. Soc. Trans. 1897, 71, 1194).

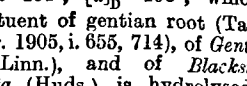
Gaultherin $C_{14}H_{18}O_8$,1Aq, decomposes at 100°, found in *Gaultheria procumbens* (Linn.), *Betula lenta* (Linn.), *Monotropa Hypopitys* (Linn.), *Spiræa ulmaria* (Linn.) *S. filipendula*, (Linn.), and other plants, forms prismatic crystals, easily soluble in water and alcohol. It is hydrolysed by mineral acids and by a specific enzyme, gaultherase, which accompanies it in plants. Emulsin is without action. The products of hydrolysis are glucose and methyl

salicylate $C_6H_4(OH)CO_2CH_3$ (*see* Bourquelot, Compt. rend. 1896, 122, 1002).

Gentiin $C_{25}H_{32}O_{14}$, m.p. 274°, occurring in the root of the gentian (*Gentiana lutea* [Linn.]), crystallises in yellow needles. It is hydrolysed to dextrose, xylose, and gentienin $C_{14}H_{10}O_5$, which is isomeric with gentisin.

Gentiopicrin $C_{16}H_{20}O_9,\frac{1}{2}Aq$, m.p. 120°–125°, or anhydrous at 191°, $[\alpha]_D$ −198°, which is likewise a constituent of gentian root (Tanret, Chem. Soc. Abstr. 1905, i. 655, 714), of *Gentiana pneumonanthe* (Linn.), and of *Blackstonia* (*Chlora*) *perfoliata* (Huds.), is hydrolysed by emulsin to dextrose and gentiogenin (comp. Bourquelot and Bridel, J. Pharm. Chim. 1910, [vii.] 1, 156).

Glucotropæolin $C_{14}H_{19}O_9NS_2K$, the glucoside of benzylthiocyanide, occurs in *Tropæolum majus* (Linn.), and *Lepidium sativum* (Linn.). It is known only in solution: with silver nitrate a precipitate is formed at first soluble in ammonia, but subsequently the ammonium compound



separates in glistening crystals. The glucoside is hydrolysed by myrosin to glucose, potassium hydrogen sulphate, and benzyl*iso*thiocyanate (Gadamer, Ber. 1899, 32, 2336). *Nasturtium officinale* (R. Br.), and *Barbarea præcox* (R. Br.), are said to contain a glucoside, *gluconasturtiin*, which differs from glucotropæolin only in yielding phenylethyl*iso*thiocyanate $C_6H_5\cdot CH_2\cdot CH_2\cdot NCS$ on hydrolysis by myrosin.

Glycyphyllin $C_{21}H_{24}O_9$, 3Aq, m.p. 175°, occurs in the leaves of *Smilax glycyphylla* (Sm.); on hydrolysis it yields rhamnose and phloretin identical with that obtained from phloridzin, in which it is combined with glucose (Wright and Rennie, Chem. Soc. Trans. 1886, 49, 857).

Gossypitrin $C_{21}H_{20}O_{13}$, m.p. 200°–202°, occurs together with quercimeritrin and *iso*quercitrin in Egyptian cotton flowers, *Gossypium herbaceum* (Linn.). It consists of pale orange-yellow needles, gives a deep red precipitate with aqueous lead acetate, and an olive-green colouration with ferric chloride (Perkin, Chem. Soc. Trans. 1909, 2181). It is hydrolysed by boiling dilute sulphuric acid to glucose and gossypetin $C_{15}H_{10}O_8$, a hydroxyflavone derivative. The glucoside exists in the flowers as a potassium salt (A. G. Perkin, Chem. Soc. Trans. 1899, 75, 825; 1902, 81, 205; 1910, 95, 1855, 2181).

Gynocardin $C_{13}H_{19}O_9N,1\frac{1}{2}Aq$, m.p. 162°, $[\alpha]_D$ +72·5°, is found in *Gynocardia odorata* (R. Br.) and *Pangium edule* (Rein.), (Power and Lees, *ibid.* 1905, 87, 349; De Jong, Rec. trav. chim. 1909, 28, 24). It is hydrolysed by acids and by a specific enzyme gynocardase to glucose, hydrogen cyanide and a complex $C_8H_6O_4$, which spontaneously resinifies.

Helicin v. *Salicin*.

Hesperidin $C_{50}H_{60}O_{27}$, m.p. 251°, $[\alpha]_D$ −89°, is found generally in the fruit of the *Aurantiaceæ*. It was discovered in unripe oranges, and occurs in most species of *Citrus* except *C. decumana* (Murr.). It is a colourless, microcrystalline, tasteless, hygroscopic powder, almost insoluble in water, readily soluble in hot acetic acid. It is faintly acid, and therefore soluble in alkalis, from which it is precipitated by carbon dioxide. It is hydrolysed by acids to glucose (2 mols.), rhamnose, and (2 mols.) hesperitin $C_{16}H_{14}O_6$, which has the structure

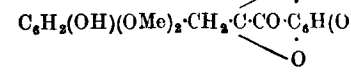
$$MeO\cdot C_6H_3(OH)\cdot CH:CH\cdot CO\cdot O\cdot C_6H_3(OH)_2,$$

and is decomposed on boiling with alkali into phloroglucinol and hydroxymethoxycinnamic acid (Will, Ber. 1887, 20, 1186; Tiemann and Will, Ber. 1881, 14, 946).

Incarnatrin $C_{21}H_{20}O_{12},3Aq$, m.p. 242°, occurs in the flowers of *Trifolium incarnatum* (Linn.), the so-called 'carnation or crimson clover' (Rogerson, Chem. Soc. Trans. 1910, 1004), and forms faintly yellow prismatic needles. It is readily hydrolysed by acids and by emulsin to glucose and quercitin.

Indican $C_{14}H_{17}O_6N,3Aq$, m.p. 100°–102°, the glucoside of woad (*Isatis tinctoria* [Linn.]) is also found in *Indigofera tinctoria* (Linn.) and other species of *Indigofera*, in *Polygonum tinctorium* (Ait.), and in *Wrightia tinctoria* (R. Br.). It is conveniently extracted from the leaf by means of acetone. It is hydrolysed by acids, by a specific enzyme, *indemulsin*, present in the leaves of the indigo plant, and more slowly by the emulsin of almonds, to glucose and indoxyl. Indoxyl (colourless) undergoes oxidation to indigotin (blue) when exposed to the air $2C_8H_7ON + O_2 = 2H_2O + C_{16}H_{10}O_2N_2$. The yield of indigotin obtained from the leaves is of great importance commercially; it is below the theoretical when hydrolysis is slow, owing to the great instability of indoxyl, and in part to the occlusion of indoxyl by the enzyme. It is improved by adding a small quantity of sulphuric acid to the mixture at the commencement of the reaction (*see* Perkin and Bloxam, Chem. Soc. Trans. 1907, 91, 715; 1909, 95, 793, 824; also references to Indican given by Armstrong, The Simple Carbohydrates and Glucosides, London, 1910).

Iridin $C_{24}H_{26}O_{13}$, m.p. 208°, occurs in the root of the violet (*Iris florentina* [Linn.]) (De Laire and Tiemann, Ber. 1893, 26, 2010), and crystallises in colourless needles, very sparingly soluble. It is hydrolysed by acids to glucose and irigenin $C_{18}H_{16}O_8$, which has the constitution:

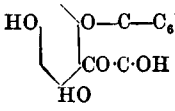


The sugar residue is attached to the hydroxyl marked *.

Jalapin (*Scammonin*) $C_{34}H_{56}O_{16}$, m.p. 131°, $[\alpha]_D$ −23°, is the active principle of the root stalks of *Convolvulus orizabensis* (Led.), and of scammony, the dried sap of *Convolvulus Scammonia* (Linn.). It is an amorphous resinous powder, translucent in thin plates; slightly soluble in water, readily soluble in alcohol and ether. It dissolves in concentrated sulphuric acid with a purple or maroon red colour, changing to brown and becoming finally black. It is hydrolysed by acids to glucose (3 mols.) and jalapinolic acid $C_{16}H_{30}O_3$, possibly hydroxyhexadecylic acid: this yields methylethylacetic acid, sebacic acid, and an isomeride of this acid on oxidation.

Jesterin $C_{26}H_{30}O_{13}$, m.p. 205°–218°, occurs in the berries of *Rhamnus cathartica* (Linn.). It is hydrolysed to a hexose, a pentose, and emodinanthranol $C_{15}H_{12}O_4$ (Krasowsky, J. Russ. Phys. Chem. Soc. 1908, 40, 1510).

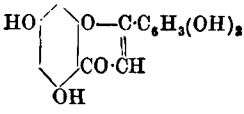
Kampferitrin $C_{27}H_{30}O_{14}$, m.p. 201°, is found in *Indigofera arrecta* (Hochst.) (Perkin, Chem. Soc. Trans. 1907, 91, 438), and forms almost colourless sparingly soluble needles; on hydrolysis rhamnose (2 mols.) and kampferol $C_{15}H_{10}O_6$ are formed—the latter has the constitution



Kampferitrin closely resembles robinin, which, according to Perkin, is also a glucoside of kampferol.

Linamarin (*Phaseolunatin*), $C_{10}H_{17}O_6N$, m.p. 141°, $[\alpha]_D$ −26°, found in *Phaseolus lunatus* (Linn.), the so-called Java beans, in flax, *Linum usitatissimum* (Linn.), and in cassava. It is hydrolysed by an enzyme, linase, present in *Phaseolus* and some *linum* species, which is allied to but not identical with emulsin, and also by mineral acids, to glucose and acetonecyanohydrin. It is a derivative of β-glucose and not of α-glucose, as originally supposed (compare Armstrong and Horton, Proc. Roy. Soc. 1910, B82, 349; Dunstan and Henry, *ibid.* 1903, 72, 285; 1906, B78, 145; 1907, B79, 315; Jorissen and Hairs, Bull. Akad. Roy. Belg. 1891, 21, 529).

Lotusin $C_{28}H_{31}O_{16}N$, obtained from *Lotus arabicus* (Linn.) (Dunstan and Henry, Phil. Trans. 1901, B, 194, 515), crystallises in pale yellow needles. It is hydrolysed by a specific enzyme, lotase, to glucose (2 mols.), hydrogen cyanide and lotoflavin, an isomeride of fisetin, which has the constitution



Apparently the hydrogen cyanide is attached to the sugar residue, as on alkaline hydrolysis heptagluconic acid is obtained.

Morindin $C_{26}H_{28}O_{14}$ or $C_{27}H_{30}O_{15}$, m.p. 245°, found in *Morinda citrifolia* (Linn.), *M. tinctoria* (Roxb.), and *M. umbellata* (Linn.), crystallises in lustrous silky yellow needles, soluble in hot water and in alcohol. It dissolves in alkalis with an orange-red colour which is not changed on boiling, and in concentrated sulphuric acid with a purple-blue colouration. It is hydrolysed by acids to a sugar which has not yet been definitely identified, and moridone, a trihydroxymethylanthraquinone, isomeric with emodin. On distillation with zinc-dust, β-methylanthracene is formed. According to Perkin, morindin from *M. citrifolia* and *M. umbellata* is not the same (*see* Perkin and Hummel, Chem. Soc. Trans. 1894, 65, 851; Thorpe and Smith, *ibid.* 1888, 53, 171; Oesterle and Tisza, Arch. Pharm. 1907, 245, 534).

Myrticolorin *v. Rutin.*

Naringin, formula uncertain +4Aq, m.p. 170°, is found in the flowers and other parts only of the Java orange, *Citrus decumana* (Murr.). It forms colourless microscopic prisms of bitter taste, sparingly soluble in water, which are strongly lævo-rotatory. It dissolves in alkalis with a yellowish red colouration and is precipitated by carbon dioxide. It is readily hydrolysed by acids to rhamnose and possibly also glucose and naringenin, which is the phloroglucinol ester of paracoumaric acid

$$C_6H_4(OH)\cdot CH : CH\cdot CO\cdot O\cdot C_6H_3(OH)_2.$$

It is closely allied to hesperitin (compare Will, Ber. 1887, 20, 297, 1186).

Osyritrin *v. Rutin.*

Phloridzin $C_{21}H_{24}O_{10},2Aq$, m.p. 108° and again 170°, was discovered in 1835 in the bark and particularly the root bark of the apple, pear, cherry, and plum tree. It forms long silky needles of bitter taste, sparingly soluble in cold, readily in hot water: it is lævo-rotatory $[\alpha]_D$ −50°. Emulsin is without action, but acids hydrolyse it to glucose and phloretin

$$C_6H_2(OH)_3\cdot CO\cdot CHMe\cdot C_6H_4(OH)$$

(Rennie, Chem. Soc. Trans. 1887, 51, 636; Fischer, Ber. 1888, 21, 988). Glycyphyllin is the rhamnose ether of phloretin.

Polygonin $C_{21}H_{20}O_{10}$, m.p. 202°, from *Polygonum cuspidatum* (Sieb. and Zucc.), crystallises in lustrous yellow needles. It is hydrolysed by acids to glucose and emodin, identical with that obtained from frangulin, where it is combined with rhamnose (Perkin, Chem. Soc. Trans. 1895, 67, 1084).

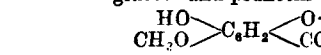
Populin $C_{20}H_{22}O_8,2Aq$, m.p. 180°, has been found in the bark and leaves of *Populus tremula* (Linn.), *P. nigra* (Linn.), and *P. balsamifera* (Linn.), and other species of *Populus*. It is prepared synthetically from salicin by heating with benzoylchloride (Schiff. Annalen, 1870, 154, 5). It crystallises in minute needles, sparingly soluble in cold water, more soluble in hot water. It is lævo-rotatory, and dissolves in concentrated sulphuric acid with an amaranth-red colouration. Emulsin is without action, but acids hydrolyse it to glucose, saligenin, and benzoic acid. Nitric acid oxidises it to benzoyl helicin (Piria, *ibid.* 1852, 81, 245; 1855, 96, 375). This proves the benzoyl group to be in the sugar and not in place of the hydroxyl as often supposed. Populin is hydrolysed by the enzyme of *Populus monilifera* (Ait.) (Weevers, Proc. K. Akad. Wetensch. Amsterdam, 1909, 12, 193).

Prulaurasin $C_{14}H_{17}O_6N$, m.p. 122°, $[\alpha]_D$ −52·75°, occurs in the leaves of the common cherry laurel, *Prunus laurocerasus* (Linn.) (Hérissey, Compt. rend. 1905, 141, 959). It is hydrolysed by emulsin and by an enzyme prunase of the emulsin type, as also by mineral acids, to glucose, benzaldehyde, and hydrogen cyanide. It is the glucoside of racemic mandelonitrile, and in view of the fact that it is readily obtained from sambunigrin or from amygdonitrile glucoside by the action of traces of alkali (Caldwell and Courtauld, Chem. Soc. Trans. 1907, 91, 671), it is not impossible that it is present in the plant in one of these active forms, and undergoes racemisation during extraction.

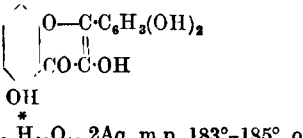
Prunasin *v. Amygdonitrile glucoside.*

Prunitrin $C_{22}H_{24}O_{11}.4Aq$, found in the bark of *Prunus emarginata* (Walp.) (Finnemore,

Pharm. J. 1910, 85, 604), is hydrolysed by acids to glucose and prunetin



Quercimeritrin $C_{21}H_{20}O_{12}$,3Aq, m.p. 247°, obtained from the flowers of *Gossypium herbaceum* (Linn.), forms small glistening bright yellow plates, almost insoluble in cold and fairly readily soluble in boiling water (Perkin, Chem. Soc. Trans. 1909, 95, 2181). The alkaline solutions are deep yellow; it gives a bright-red precipitate with aqueous lead acetate. It is very stable towards mineral acids, but is eventually hydrolysed to glucose and quercetin. The glucoside exists in the flowers in a readily soluble condition in the form of a potassium salt. Quercimeritrin contains the quercetin hydroxyl groups in the 3', 4', and 3- positions intact, the sugar residue R being united to one of the hydroxyl groups marked *



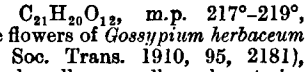
Quercitrin $C_{21}H_{20}O_{11}$,2Aq, m.p. 183°–185°, or anhydrous 250°–252°, $[\alpha]_D$ −140·9°, found in the bark of *Quercus discolor* (Ait.) and elsewhere; crystallises in bright-yellow lustrous needles, almost insoluble in cold, sparingly soluble in hot water, and easily soluble in alcohol. It shows an intense green colouration with ferric chloride. Emulsin is without action, acids readily hydrolyse it to rhamnose and quercitin (tetrahydroxyflavonol). In quercitrin, the sugar group is not attached to the phloroglucinol residue, but to one or other of the three remaining hydroxyls (Hlasiwetz and Pfaundler, Ann. 1863, 127, 362; Liebermann and Hamburger, Ber. 1879, 12, 1178, &c.)

***iso*Quercitrin** $C_{21}H_{20}O_{12}$, m.p. 217°–219°, also found in the flowers of *Gossypium herbaceum* (Perkin, Chem. Soc. Trans. 1910, 95, 2181), crystallises in pale-yellow needles almost insoluble in cold and but sparingly in boiling water. With lead acetate it gives a bright-yellow precipitate, very different from the deep-red deposit produced from quercimeritrin. The glucoside is isomeric with quercemeritrin, and, like it, yields glucose and quercetin on hydrolysis, but differs in being readily attacked. The shades produced with the glucoside on mordanted wool closely resemble those yielded by quercitrin, but are entirely distinct from those given by quercimeritrin. The sugar is attached to either the 3', 4', or 3- positions, and not to the phloroglucinol nucleus.

Quinovin (*Chinovin*) $C_{30}H_{48}O_8$ or $C_{36}H_{62}O_{11}$, α-quinovin accompanies the cinchona alkaloids; it is obtained from the bark of *China nova*, which, after extraction with water, is boiled with milk of lime. The glucoside is precipitated on the addition of hydrochloric acid, and after purification forms a colourless crystalline powder, $[\alpha]_D$ +59·1°: it is almost insoluble in water, and has a bitter taste. Alcoholic hydrogen chloride hydrolyses it to quinovaic acid $C_{24}H_{38}O_4$, and a methyl pentose, quinovose (*v.* CARBOHYDRATES), which, however, under these conditions, is converted into the glucoside ethylquinovoside (quinovite) $C_6H_{11}O_4{\cdot}OC_2H_5$. β-Quinovin is found in the *Remijia* species, and crystallises in plates, m.p. 235°, $[\alpha]_D$ +27·9°: it yields the same products on hydrolysis (compare Hlasiwetz, Ann. 1859, 111, 183; Rochleder, Zeitsch. Chem. 1867, 357).

Robinin $C_{33}H_{40}O_{19}$, the glucoside of the white azalea, *Robinia pseud-acacia* (Linn.), yields, on hydrolysis, galactose, rhamnose (2 mols.), and a yellow colouring matter robigenin $C_{15}H_{10}O_5$, closely related to quercetin (Schmidt, Arch. Pharm. 1904, 242, 210; Perkin, Chem. Soc. Trans. 1902, 81, 473).

Ruberythrinic acid $C_{26}H_{28}O_{14}$, m.p. 258°, is the constituent of madder root, *Rubia tinctorum* (Linn.), which, on hydrolysis, yields alizarin. It crystallises in citron-yellow needles, sparingly soluble in cold water. It dissolves in concentrated sulphuric acid, and in alkalis with a bright-red colouration. Acids and the enzymes of madder hydrolyse it to glucose (2 mols.) and alizarin (dihydroxyanthraquinone). Since the glucoside is acid, the two glucose molecules are probably united as a disaccharide, and not attached to both hydroxyl groups. The formula



thus represents the glucoside (Liebermann and Bergami, Ber. 1887, 20, 2241; Schunck and Marchlewski, Chem. Soc. Trans. 1894, 65, 182).

Rubiadin glucoside $C_{21}H_{20}O_9$, m.p. 270°, also present in madder, forms yellow needles, which are hydrolysed to glucose and methyldihydroxyanthraquinone (Schunck and Marchlewski, Chem. Soc. Trans. 1893, 63, 969, 1137).

Rutin $C_{27}H_{30}O_{16}$,3Aq, m.p. 184°, originally discovered in rue, *Ruta graveolens* (Linn.); also occurs in *Fagopyrum esculentum* (Moench), *Capparis spinosa* (Linn.), *Globularia Alypum* (Linn.) *Colpoon compressum* (Berg.) *Eucalyptus macrorhyncha* (F. Muell.), *Viola tricolor* (Linn.), *Tephrosia purpurea* (Pers.), &c.; it is identical with glucosides described as violaquercitrin, osyritrin, myrticolorin. It forms pale-yellow lustrous needles sparingly soluble in cold water and alcohol, more soluble on heating. It is hydrolysed with some difficulty to glucose, rhamnose, and quercitin (compare Schmidt, Arch. Pharm. 1904, 242, 210; 1908, 246, 214; Wunderlich, *ibid.* 1908, 246, 224, 241).

Sakuranin $C_{22}H_{24}O_{10}$,4Aq, m.p. 210°–212°, the glucoside of *Prunus paniculata* (Thunb.) the Japanese cherry tree, forms colourless bitter needles, and yields glucose and sakuranetin $C_{16}H_{14}O_5$, m.p. 150°, on hydrolysis. It is physiologically inert. Sakuranetin contains one methoxyl group, absorbs bromine, and yields phloroglucinol, acetic, and *p*-hydroxybenzoic acids when fused with potash (Asahina, Arch. Pharm. 1908, 246, 259).

Salicin $C_{13}H_{18}O_7$, m.p. 201°, $[\alpha]_D$ −65°, is the bitter stuff of willow bark, and was formerly used as a remedy against fever. It is found in many but not all salix species, and besides the bark it occurs also in the leaves and female flowers. The amount varies according to the time of year. It occurs also in poplars and in the flower buds of meadow-sweet, *Spiræa Ulmaria* (Linn.). It crystallises in needles, plates, or rhombic prisms. It dissolves in about 30 parts of cold water, easily in hot water. The solutions

taste bitter and are lævo-rotatory It dissolves in concentrated sulphuric acid with an intense red colouration: this is the so-called 'rutilin' reaction. Emulsin readily hydrolyses it to glucose and saligenin (*o*-hydroxybenzyl alcohol). It is also hydrolysed by a specific enzyme salicase present in willow leaves and twigs.

Benzoyl salicin is the natural glucoside *populin*. Mild oxidation with dilute nitric acid converts the primary alcohol group of salicin into aldehyde, forming *helicin* $C_{13}H_{16}O_7$; *e.g.*

$$C_6H_4(OC_6H_{11}O_5)CHO.$$

This forms bunches of slender needles, m.p. 174°. Emulsin hydrolyses it to glucose and salicylaldehyde. Helicin was synthesised by Michael by the interaction of acetochloroglucose and potassium salicylaldehyde.

Salinigrin $C_{13}H_{16}O_7$, m.p. 195°, $[\alpha]_D$ −87·3°, found only in *Salix discolor* (Muhl.) (Jowett and Potter, Pharm. J. Aug. 16, 1902), is the glucoside of *m*-hydroxybenzaldehyde, an isomeride of helicin. It gives no colour with sulphuric acid.

Sambunigrin $C_{14}H_{17}O_6N$, m.p. 151°, $[\alpha]_D$ −76°, is present in the leaves of the elder, *Sambucus nigra* (Linn.). It is isomeric with amygdonitrile glucoside, although, like this, it is hydrolysed by emulsin, the products being glucose and *l*-mandelonitrile, *i.e.* the nitrile of *d*-mandelic acid (Bourquelot and Danjou, Compt. rend. 1905, 141, 59, 598).

Saponins $C_nH_{2n-8}O_{10}$ are a class of closely analogous glucosides, very widely distributed in plants, having the property of dissolving in water, giving clear solutions which froth strongly on agitation, form emulsions with oils and resinous substances, and prevent the deposition of finely divided precipitates. They have a bitter acrid taste, and the dust is very irritating and sternutatory: they are colloids and not dialysable. The more poisonous are distinguished as sapotoxins. They are hydrolysed by dilute acids to glucose, galactose, and active substances termed sapogenins: the different saponins give different proportions of sapogenin and sugar.

Saponins are prepared by extraction with water and precipitation with neutral lead acetate, if acid saponins are present: basic lead acetate is then added to the filtrate to precipitate the neutral saponins. The precipitates are decomposed and the saponin solutions evaporated, the residue being purified by solution in chloroform and precipitation by ether. For further purification, the saponin is precipitated by barium hydroxide, and the barium compound decomposed by carbon dioxide.

Saponins form double compounds with cholesterol (*v. Digitonin*). The best-known saponins are:

Quillaic acid $C_{19}H_{30}O_{10}$, the acid glucoside obtained from the bark of *Quillaja Saponaria* (Molina), is a constituent of commercial saponin. The pure glucoside is non-poisonous: it forms white flakes, which become red on treatment with strong sulphuric acid.

Quillaia sapotoxin $C_{17}H_{26}O_{10}$, derived from the same source, is a colourless amorphous powder possessing poisonous properties.

Saporubrin $(C_{18}H_{28}O_{10})_4$, the sapotoxin from the root of the soapwort, *Saponaria officinalis* (Linn.), has $[\alpha]_D$ −54°. It yields a series of sapogenins on hydrolysis, each giving up a further molecule of sugar as the treatment with dilute acid is continued. The final product has the formula $C_{14}H_{22}O_2$.

Levant sapotoxin $(C_{17}H_{26}O_{10},H_2O)_2$ from the root of *Gypsophila Arrostii* (Guss.) or *G. paniculata* (Linn.), is very similar to saporubrin. On hydrolysis, 4 mols. sugar (56 p.c.), probably a mixture of glucose and galactose, and a sapogenin $C_{10}H_{16}O_2$ (23 p.c.), are formed.

Agrostemma sapotoxin $(C_{17}H_{26}O_{10})_2$, from the corncockle, *Lychnis* (*Agrostemma*) *Githago* (Scop.) is a yellowish-white amorphous powder yielding 4 mols. sugar and a sapogenin $C_{10}H_{16}O_2$ on hydrolysis. It is absorbed by both the subcutaneous tissue and the intestines, and is therefore a dangerous poison.

Parillin $C_{26}H_{44}O_{10}$, one of the saponin glucosides of sarsaparilla, the dried root of various *smilax* species, has m.p. 177°, $[\alpha]_D$ −42°. It is hydrolysed to a mixture of two sugars and parigenin $C_{26}H_{46}O_4$. The other glucosides of sarsaparilla are *smilasaponin* $(C_{20}H_{32}O_{10})_5$ and *sarasaponin* $(C_{22}H_{36}O_{10})_{12}$, m.p. 223°.

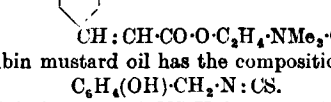
Scopolin $C_{22}H_{28}O_{14}$,2Aq, m.p. 218°, occurs in *Scopolia japonica* (Maxim.) and *S. carniolica* (Jacq.). It is hydrolysed to glucose (2 mols.) and scopoletin, which is identical with æsculin methyl ether (Eykman, Rec. trav. chim. 1884, 3, 177).

Serotin $C_{21}H_{20}O_{12}$,3Aq, m.p. 245°, found in the leaves of *Prunus serotina* (Ehrh.), commonly known as the wild black cherry, crystallises in golden yellow leaflets. It is more soluble in water and more readily hydrolysed than quercimeritrin. Acids convert it into glucose and quercitin (Power and Moore, Chem. Soc. Trans. 1910, 97, 1099).

Sinalbin $C_{30}H_{42}O_{15}N_2S_2$,5Aq, m.p. 138°–140°, found in white mustard *Sinapis alba* (Linn.), crystallises in faintly yellow-coloured needles which are slightly soluble in cold, easily soluble in hot water, and lævo-rotatory. It is hydrolysed by the myrosin present in the seeds to glucose, sinalbin mustard oil $C_7H_7O{\cdot}NCS$, and acid sinapin sulphate $C_{16}H_{24}O_5N{\cdot}HSO_4$. Sinapin $C_{16}H_{25}O_5N$ is only known in the form of its salts, barium hydroxide converts it into choline $C_2H_4(OH)N(OH)Me_3$ and sinapinic acid

$$C_6H_2(OH)(OMe)_2CH:CH{\cdot}CO_2H.$$

The alcohol corresponding to this acid is syringenin obtained from the glucoside syringin. Sinapin is accordingly



$$CH:CH{\cdot}CO{\cdot}O{\cdot}C_2H_4{\cdot}NMe_3{\cdot}OH.$$

Sinalbin mustard oil has the composition

$$C_6H_4(OH){\cdot}CH_2{\cdot}N:CS.$$

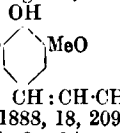
Sinigrin $C_{10}H_{16}O_9NS_2K$,Aq, m.p. 126°, is the active principle of black mustard, *Brassica nigra* (Koch). It crystallises in lustrous colourless needles, very soluble in water, sparingly soluble on cold alcohol. It is lævo-rotatory. Myrosin or a water extract of the seeds hydrolyses it to glucose, allyl*iso*thiocyanate and potassium hydrogen sulphate. Emulsin is without action. As hydrolysis by myrosin proceeds, the increasing

quantity of acid potassium sulphate formed renders the ferment less active and ultimately stops its action. Gadamer has proposed the formula, $C_3H_5N:C(SC_6H_{11}O_5)O(SO_3K)$.

Skimmin $C_{15}H_{16}O_8$, m.p. 210°, occurs in *Skimmia japonica* (Thunb.). It crystallises in colourless needles, sparingly soluble in water, and dissolves in alkalis with a blue fluorescence. Acids hydrolyse it to glucose (?) and skimmetin ($C_9H_6O_3$), m.p. 223°, which is perhaps identical withumbelliferone(monohydroxycoumarin)(Eykman, Rec. trav. chim. 1884, 3, 208).

Strophanthin $C_{40}H_{66}O_{19}$, m.p. 170°–172°, is obtained from the seeds of *Strophanthus Kombe* (Oliver) and other species. It occurs as a pale-yellow amorphous or a colourless microcrystalline powder, having an intensely bitter taste and a faintly acid reaction. It is freely soluble in water and very poisonous. With concentrated sulphuric acid it is coloured green or orange, then red, and, on warming, dark-brown and finally green. Acids hydrolyse it to strophantidine $C_{27}H_{38}O_7$, and methyl strophantobioside $C_{13}H_{24}O_{10}$, which is in turn broken down to rhamnose, mannose, and methyl alcohol. Strophantin is similar to digitalis in its action on the heart.

Syringin $C_{17}H_{24}O_9$,1Aq, m.p. 191°, $[\alpha]_D$ −17°, is found in the syringa, *Syringa vulgaris* (Linn.), and also in the bark of lilac and privet. It crystallises in slender needles, gives a reddish-violet colouration with sulphuric acid, and is readily soluble in warm water. It is hydrolysed by emulsin and by acids to glucose and syringenin, *i.e.* dimethoxyconiferyl alcohol



(*see* Körner, Gazz. chim. ital. 1888, 18, 209).

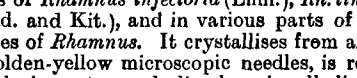
Trifolin $C_{22}H_{22}O_{11}$,1Aq, m.p. 260°, found in the flowers of the common red clover, *Trifolium pratense* (Linn.), forms slender pale-yellow needles. It gives intense yellow solutions with alkalis, gives a yellow solution which develops a green fluorescence in concentrated sulphuric acid. It is hydrolysed by acids to rhamnose and trifolitin $C_{16}H_{10}O_8$, a yellow colouring matter (Power and Salway, Chem. Soc. Trans. 1910, 97, 231).

Turpethin $C_{34}H_{56}O_{16}$, m.p. 149°, from the dried sap or root of *Ipomoea Turpethum* (R. Br), is very similar to jalapin, but differs in being insoluble in ether. It is an amorphous powder. Acids hydrolyse it to glucose (3 mols.), turpethol $C_{16}H_{30}O_3$, *iso*butyric acid, and a viscid acid, $C_{15}H_{28}O_5$ (*see* Spirgatis, Annalen, 1866, 139, 41; and Kromer, Chem. Soc. Abstr. 1893, i. 482). Votoček and Kastner (Chem. Soc. Abstr. 1907, i. 330) have isolated two other glucosides, α- and β-turpethein from *I. turpethum*. The α-isomeride gives rhamnose, the β-isomeride rhodeose, and glucose when hydrolysed.

Vicianin $C_{19}H_{25}O_{10}N$, m.p. 160°, $[\alpha]_D$ −20°, occurs in the seeds of *Vicia angustifolia* (Bertrand and Weisweiler, Compt. rend. 1908, 147, 252; 1910, 151, 325). It is hydrolysed by an enzyme present in many vicia species to *d*-mandelonitrile and a C_{11} disaccharide (vicianose), which is composed of glucose and arabinose. Vicianin therefore represents an amygdalin in which arabinose is substituted for glucose.

Violaquercitrin *v. Rutin.*

Xanthorhamnin $C_{34}H_{42}O_{20}$ is found in the fruits of *Rhamnus infectoria* (Linn.), *Rh. tinctoria* (Wald. and Kit.), and in various parts of other species of *Rhamnus*. It crystallises from alcohol in golden-yellow microscopic needles, is readily soluble in water and dissolves in alkalis with a yellow colouration. It is hydrolysed by an enzyme *rhamninase* to a trisaccharide (rhamninose) and rhamnetin $C_{16}H_{12}O_7$. Rhamninose is further hydrolysed by acids to rhamnose (2 mols.) and galactose. Rhamnetin is quercitin monomethyl ether



(*see* Tanret, Compt. rend. 1899, 129, 725). E. F. A.

GLUCURONIC ACID *v.* CARBOHYDRATES.

GLUE AND GLUE TESTING. The term *glue* comprises preparations obtained by the action of water from certain portions of animals and fishes, which have the power of gelatinising in aqueous solution and drying up to a hard strongly adhesive layer.

Other preparations which possess this adhesive property are also loosely termed glues; *e.g.* marine glue, a resinous composition; gluten and casein glues, mineral and vegetable glues, &c., but, strictly speaking, they have no claim to that name, as they contain no gelatin.

The term *gelatin* is applied to glues made from specially selected stock, and so gelatin may be considered a purer form of glue.

Glue or gelatin is probably not contained as such in the animal, but is the product of the hydrolysis of various nitrogenous tissues, brought about by boiling with water.

These tissues have been classed as follows:—

(1) *Ossein*, of bones and skin, *Chondrigen*, of cartilage; *Isinglass*, from the bladders of fish: these are classed under the general name of *Collagens*.

(2) *Elastin*, from certain ligaments.

(3) *Chitin*, from beetles, locusts, shrimps, crabs, &c. It can be converted into a gelatinous form by treatment with acids, but is of no utility.

(4) *Keratin*, from hair, horns, hoofs, and feathers. These yield products which have little power of gelatinising, and are not used in the glue manufacture.

For convenience the products obtained from collagens by the action of water may be classed into Glutin and Chondrin, the properties of which will be described later.

Manufacture.—(*a*) **Bone glue.** For this purpose, bones of all kinds are used, and vary, therefore, so much in composition that it is useless to give any detailed analysis. In addition to calcium phosphate and carbonate, the main ingredients of the ash, they contain fat and gelatin-forming substances, ossein and chondrin. Before the gelatin can be obtained, it is necessary to remove the fat of which fresh bones such as ribs, heads, shoulder blades, contain from 12 to 13 p.c., while large thigh bones may contain 17 to 18 p.c. Marine store bones, such as have been used for soup, Indian and South American bones rarely contain more than 12 p.c. of fat.

There are in use three chief methods of extracting the fat :—

(1) By simply heating the bones in a tank provided with a steam coil ; (2) by heating with steam in a digestor under pressure ; (3) extraction of the fat by volatile solvents.

By the first of these processes, the yield is only about 5 p.c., by the second 7 to 8 p.c., whilst by the third almost all the fat can be obtained.

The solvent extraction process is the one now used in most modern factories. The solvents are mainly those portions of Scotch shale naphtha or American or Russian petroleum, boiling from 100° to 138°, and coal-tar naphtha of similar boiling-point. In this country, Scotch shale naphtha, boiling between 100° and 115°, is usually employed. A modern extracting plant consists of, say, 6 cylindrical vertical boilers of a capacity of 5 tons of bones, worked in sets of three, one lot extracting while the other set is being emptied. As the bones are delivered at the works, they are sorted and then crushed in a mill and filled into the extractors, which are provided with perforated false bottoms, under which are placed wet and dry steam coils. At the top of each is a pipe for conveying off the vapour of the solvent to a set of condensers usually placed outside the building. When the extractors have been filled and the manholes closed, the solvent is run in and heat applied by the dry coils until the solvent begins to distil over, carrying with it the moisture present in the bones. When it begins to pass over free from moisture, the dry coils are shut off, and the first charge of the extracted fat run off from below the bones into the *mont-jus* or 'distiller.' This operation is repeated three or four times, when the bones are free from fat, but retain a considerable amount of the solvent, which is blown over by high-pressure steam from the wet coils into the condenser. The whole operation takes about 12 hours. The bones are then raked out through the lower manhole and conveyed to the cleanser. When dry, they should be free from smell, and contain not more than ½ p.c. of fat. The fat held in solution in the solvent is then heated in the distiller to expel the solvent which is condensed and used again. The fat is freed from dirt by heating with hot water and settling, and is then run into barrels. It contains about 98 p.c. of pure fat and is used in soap, candle, glycerol, and in the case of fresh bones for margarine making.

The cleansing of the bones is done by passing them through a rotating cylindrical wire gauze sifter, and they are then ready for the boiling operation.

The extraction or 'cooking' is carried out in one of two ways : (1) By the alternate action of steam and water playing on the bones contained in a large iron boiler of from 3 to 5 tons capacity. As this method yields weak glue solutions, costly to concentrate, modern manufacturers prefer the second plan (2) *i.e.* to 'cook' in autoclaves under, say, 15 lbs. steam pressure, reduced later to 4 to 5 lbs., this being done to allow the glue contained in the interior of the bones to exude, so that it may be washed down by the spray of water. This action is repeated until the solution contains about 20 p.c. of glue.

The glue liquors are then clarified by standing in tanks, kept warm by steam coils, when the dirt settles, and any grease rising is skimmed off. To assist in the clarification, many substances have been suggested, such as blood, basic lead acetate, milk of lime, sodium phosphate, oxalic acid, albumen, but they are rarely used, as ½ p.c. of potash alum fulfils the purpose better than any of them. After adding the dissolved alum, the whole mass is agitated and heated to 80°, and then strained through fine wire gauze or canvas.

The glue solution, thus clarified, is then introduced into the concentrators, where excess of water is removed under reduced pressure, so as to avoid injury to the glue by heating to too high a temperature.

The principle of these concentrators is that of the vacuum pan, and the Yaryan type is one of the most modern forms.

This consists of an iron vessel, globular or cylindrical in shape, steam jacketed and provided internally with steam coils immersed in the glue solution. The dome, which is provided with baffle plates, is connected with a vacuum pump and condenser. In order to save fuel, the steam from the glue of one pan is led on the multiple-effect principle, into the coils and jacket of another, and so on to a third. (*V.* EVAPORATION.)

After concentration, the glue liquors, before settling, are usually bleached by the action of sulphur dioxide, produced in any suitable way, which is led through the liquors by perforated pipes while they are contained in lead-lined tanks and kept liquid by steam coils. When the required shade has been reached, the liquors are ready for jellying, and are run out into galvanised iron troughs, 2 feet × 6 inches, to the depth of 5 inches, and allowed to cool. When set, the mass is removed and cut by a 'wire knife' into sheets of suitable thickness. Or the troughs may be dispensed with and the liquid jellied on water-cooled glass slabs placed in rows on tables.

The drying operation, which follows, is one of the most important parts of the manufacture of glue. Since the jelly melts at a temperature of about 25° in summer, the air entering the drying rooms must be cooled, while in winter it is usually so charged with moisture that, in order to effect any desiccation of the jelly it must be warmed. These operations are carried out by suitable refrigerators and steam pipes.

The cakes of glue are placed on frames covered with nets, which may be of cotton or wire. These are supported on suitable trollies and placed in chambers through which air, of the proper temperature and humidity, as indicated by wet-and-dry bulb thermometers, is circulated by fans. In 4 or 5 days, the cakes are removed from the racks and packed; they then contain 10 to 13 p.c. of water.

Osseine is a French preparation obtained by treating the fat-freed bones with dilute mineral acids, when the phosphates and other soluble salts are removed.

The residue consists of the glue-forming ingredients of the bones, and may be made into glue by treatment with water under heat, but in the writer's experience, the change is very

slow, and the preparation, although useful to the manufacturer of glue, is not to be recommended to the ordinary consumer of size.

Hide or Skin glue. While the *epidermis* of the hide yields little or no glue, the *corium*, or inner skin, consisting mainly of connective tissue, gives a good percentage on treatment with hot water.

The raw materials for skin glue are the various clippings of hides, the ears and tails of oxen and sheep, rabbit and hare skins, old parchment, old gloves, pigs' skins, and all waste leather which has not been tanned.

The first process in the manufacture of glue from these is to subject them to the action of milk of lime in shallow pans or pits for several days, the skins being constantly stirred with forks.

These operations loosen the hair. From the pits, the skins are taken to the unhairing room, where the still adhering hair is scraped off by a blunt knife, and any fleshy parts, &c., removed. The hair thus obtained finds use in plastering work and felt making, etc.

Tanned leather cannot be used, but tannery waste trimmings, after the liming or depilatory process, form the raw material for good glue.

In modern practice, besides milk of lime, other substances, such as sodium sulphide, soda, and a mixture of soda and lime are used. The first is said to be good, but in presence of iron causes blackening of the hides.

After liming, the skins, when firm and free from greasy feel, are washed, first with water, then with dilute hydrochloric acid, and finally again with water. The excess of water is removed from the wet stock by drying and pressing.

The dried material is then heated, enclosed in sacks in a boiler with water until the liquors contain about 32 p.c. of glue. It may then be run in a Yaryan concentrator, or direct into coolers, or on to glass slabs for jellying and cutting and dried as before.

Fish glue. The raw materials for this are chiefly the skins (especially those of soles and plaice), the bladders of various fish and all varieties of fish offal. These yield, by processes similar to the above, a very adhesive but evil-smelling glue, which it is said may be deodorised by treatment with 1 p.c. of sodium phosphate and 0·25 p.c. of *saccharine* (Lambert).

Isinglass is a valuable product obtained from the swimming bladders of various fish, of which the sturgeon of the Volga yields the best quality, but Brazilian, Penang, Indian, and Hudson's Bay isinglass are also on the market. It arrives in this country either as the unopened bladders, known as pipe isinglass, or as purse, lump, or leaf. In preparing the last two, the bladders are cleansed by washing with hot water, and then cut open and dried.

Before solution in water, the crude isinglass is moistened, cut into strips, rolled out into ribbons and dried. When dry they are shredded by suitable machines. Isinglass is mainly used in clarifying wines, ciders, and beers, by the cook for making jellies, and in the preparation of plasters.

Glue size may be considered as a by-product, since it usually consists of the crude glue liquors which are the product of the third or fourth extraction of the raw material, which, if dried, would yield a glue of inferior quality. In small works and in some factories, where size is used, it is often made direct from bones or such leather waste as 'pickers' by treatment with lime, heating and straining.

Size is usually treated with sulphur dioxide to improve its colour and its keeping power. Zinc sulphate or boracic acid is often added as a preservative, and when sold it usually contains about from 25 to 38 p.c. of glue.

Concentrated size consists of ground glue, such cakes as are off shade and quality being used.

Coloured or Opaque glues are made by the addition of a small quantity of some pigment such as finely ground chalk or whitening.

Chemistry and Properties of Glue.

The products yielded by the hydrolysis of collagens may be divided into three groups:

(1) **Glutin (gelatin).** This is a colourless, yellowish, transparent, odourless, and tasteless body. It has the following composition:—

Gelatins from Connective Tissue.
(Chittenden, 1908.)

	1	2
Carbon	50·12	50·00
Hydrogen	6·68	6·52
Nitrogen	17·84	17·88
Sulphur	0·32	0·23
Oxygen	25·10	25·35
Ash	0·32	0·36

The quantity of sulphur varies considerably, and appears to be largely a constituent of the ash, which, in commercial glue, is often as high as 1·75 p.c. By precipitation with alcohol from aqueous solution, gelatin may be obtained almost ash- and sulphur-free. When immersed in water, glutin, while insoluble in the cold, swells up and greatly increases (5 or 6 times) in weight. It dissolves in hot water, and the solution, on cooling, sets to a jelly. Prolonged heating with water lessens its gelatinising power. Solutions of glutin on exposure to air rapidly putrefy, evolving, among other products, ammonia. It is insoluble in ether and alcohol, but soluble in glacial acetic acid (such solutions being made use of in the familiar 'Diamond cement' and 'Seccotine'). Solutions of glutin are not precipitated by gold, silver, or copper salts, but the two former are reduced to the metallic state on heating. Platinum salts give brown precipitates and form a delicate test for glutin. The various tannic acids precipitate glutin, with the production of leather-like substances. This precipitate is insoluble in organic solvents, such as ether and alcohol, but soluble in warm alkalis. Iron, aluminium, potassium, and lead salts cause no precipitate, but mercuric chloride renders its solution turbid. Chromium salts, especially potassium dichromate and chrome alum, have the power of rendering gelatin insoluble in water after exposure to light, which property is made use of in photography and other industries.

Dry distillation of glutin yields water and a dark thick oil, similar to Dippel's oil, containing pyridene bases, aniline, &c. Formaldehyde, when added to a glutin solution, solidifies it and renders it no longer soluble even in hot water. 8 p.c. of formaldehyde on the dry glue gives maximum effect. This property has been

utilised in waterproofing and in the production of Vandura silk.

(2) **Chondrin.** This horny substance, very similar to glutin, is contained in most glues, but differs in being precipitated from its solutions by nearly all acids, though usually soluble in excess. Many salts, such as alum, lead acetate, and iron salts, also precipitate it. Its composition is given as:

Carbon	49·92
Hydrogen	6·76
Nitrogen	15·65
Oxygen	27·67

Its gelatinising and adhesive powers are weaker than those of glutin.

(3) **Mucin.** This name covers a number of bodies which are usually removed in the liming operation. If left in the glue, they give rise to 'foaming,' and have little or no adhesive property.

Uses of glue.—A great variety of industries employ glue in some form or other. It is employed in sizing textiles, papers, walls, canvas, &c. It is also largely employed in joiners' work, veneering, box making, the making of matches, &c.

Mixed with glycerin, treacle, or glucose, it forms the compositions used as substitutes for rubber and for printing rollers, stamps, &c. Mixed with treacle or glycerin, it is employed in making the familiar 'jellygraph.'

It is also used in photography, and as gelatin it forms part of the raw materials of cookery.

Glue Testing.

The testing of glue has relation to the properties required for the particular purpose to which the glue is to be put. General requirements are tenacity, adhesiveness, and keeping power.

Chemical tests. (1) *Moisture determination.*—The sample of glue is reduced to shavings by means of a 'spoke-shave,' and these are ground to powder in a mortar. Five grams are weighed out on to a clock-glass and dried, first in the water-oven and then in a toluene bath to constant weight. Glues in this way yield 12 to 18 p.c. of moisture. A very low result is not desirable, as it shows the glue has been over-dried and has little tenacity, while a high result throws doubts on its keeping quality.

(2) *Ash.*—A portion of the glue is incinerated in a platinum crucible, and the ash weighed. That from bone glue fuses and gives, when taken up in dilute nitric acid, the phosphoric acid reaction with ammonium molybdate, whereas the ash from hide glue does neither, and is usually alkaline from the lime used in the preparation. The ash content of good glues varies from 1·5 to 3·0 p.c. Glues weighted with barytes, &c., and 'coloured glues,' of course, yield more.

(3) **Acidity** may be determined directly by titrating a measured quantity of, say, a 10 p.c. solution with standard alkali, using phenolphthalein as indicator. Should the glue solution be highly coloured, as is the case with some Scotch glues, fluorescein may be used in its place. The volatile acids of glue may be determined by dissolving 50 grams of the sample in water, and subjecting the solution to steam distillation. The steam and vapour are led through a condenser and received in a vessel containing a known volume of standard alkali. After some 300 c.c. have been condensed, the amount of acid absorbed by the alkali is determined by titration. It is expressed as H_2SO_3, and a good glue should not yield more than 0·2 p.c. (Lambert).

(4) **Fatty matters** are determined by extracting 5 grams of the finely powdered sample, contained in a capsule in the Soxhlet apparatus with ether.

(5) **Determination of the gelatin content by yield of nitrogen.** Trotman and Hackford (J. Soc. Chem. Ind. 1904, 1072) give a process for the determination of the gelatin present in glue. They point out that a direct determination of nitrogen by Kjeldahl's method or soda lime distillation gives misleading results—owing to the presence of peptones, &c. (the decomposition products of gelatin) when it is multiplied by the factor 5·33. They consequently precipitate the gelatin with zinc sulphate crystals, wash the precipitate with concentrated zinc sulphate solution, and treat the product by the Kjeldahl process. The amount of nitrogen, multiplied by 5·33, gives the gelatin content. This method has been criticised by H. J. Wilson, but it appears to differentiate between gelatin and the other nitrogenous ingredients of glue.

Estimation by precipitation with tannic acid. Standard solutions of pure gelatin (10 grams per litre) and of tannic acid (10 grams per litre) are made. The two are then titrated together until no further precipitate is produced. A weighed quantity of the sample is then titrated against the tannic acid, and thus its gelatin content determined.

Stelling's method of determining gelatin consists in precipitating the solution by 96 p.c. alcohol, but owing to the partial solubility of gelatin in that menstruum, Rideal considers it untrustworthy.

(6) **Water absorption.** A very general method of testing glue consists in determining the amount of water which it will absorb. A weighed quantity of glue is covered with water at 60°F. (15·5°C.) and allowed to soak for from 24 to 48 hours, according to the thickness of the cake, or until the cake is thoroughly saturated by the water, which can be judged by its colour and appearance.

The cake is then removed, dried superficially with filter paper, and the increase of weight determined. Generally speaking, the greater the increase the better the glue, provided that the cake remains firm. Fine bone and skin glues will increase in weight 8 to 11 times, common glues 5 times, but some of the very common fish glues may liquefy completely under these conditions. In making this test, the smell of the glue and the colour of the water should be noted, when valuable information as to the keeping qualities and probable sources of the glue may be gleaned.

Jelly tests. 10 grams of glue are soaked for 24 hours in water, and then melted and the solution made up to 100 c.c. The solution is cooled, and the strength of the jelly tested with the finger. It is quite possible to grade the various samples of glue with considerable accuracy by this method.

Lipowitz shot test. If it is desired to have a quantitative expression of the strengths of the jellies yielded by a number of samples of glue, the samples containing 10 p.c. of glue may be run into cylinders of uniform width and allowed to set. The cylinders are then in turn covered with a lid, through which, in a guide tube, passes a stout wire, to the lower end of which is soldered a convex disc, while the upper end carries a pan to carry weights or shot. The convex surface of the disc rests on the surface of the jelly, and weights or shot are added to the upper pan until the lower disc penetrates. The greater the amount of weight the jelly will carry, the greater is its consistency.

This method is largely employed, but its value is only comparative.

Strength of jelly. The writer has used a method for some years which he claims to give more reliable results. 30 grams of glue are soaked in water and, after melting, the solution is made up to 100 c.c. and transferred to a vessel so that the depth of the layer is 1½ to 2 inches. This, of course, may be varied according to the vessels at command, but it should be the same for all the samples. While the solution is still warm, a circular disc of metal 1 inch in diameter, to the centre of which is fixed a stout wire, is inserted. Halfpennies form convenient discs. The wire is kept in a vertical position until the solution has jellied. The vessel is clamped down and the wire attached to one arm of a stout balance. Weights are then placed in the other pan until the disc is torn through the jelly. The greater this weight, the tougher the jelly and stronger the glue. The test should be repeated several times, and the mean taken. A good glue under these conditions requires over 10 lbs. to tear the disc through the jelly. It is claimed that by this method the variations due to the surfaces of the glue jellies are obviated.

Melting-point of jelly. 15 grams of the sample are soaked in 30 c.c. of water for 12 hours, heated on the water-bath, and the solution poured into a wide test-tube in which a thermometer is inserted. In a similar tube, a solution of a good hide glue (1:1) is poured, and both tubes are immersed into water at 15°. When set, the two tubes are placed in a horizontal position on a shelf over a water-bath. Their melting-point is taken to be the temperature at which the surfaces of the glue solutions leave their vertical positions (Kissling).

Viscosity of jelly Fels (J. Soc. Chem. Ind. 1901, 139) recommends that the viscosity of a 15 p.c. solution of glue at 30° should be tested in the Engler viscosimeter, on the assumption that the greater the viscosity the stronger is the glue.

Rideal uses a modified form of the Slotte instrument (J. Soc. Chem. Ind. 1891, 615), and uses 1 p.c. solutions at 18°.

A simple way of carrying it out is to run the solution from a burette; the time taken for 50 c.c. to flow is taken as a measure of its viscosity. Supposing 25 secs. are taken by water at that temperature, a 1 p.c. solution of a strong glue will take 32 to 34 secs.; a medium glue, 28–30 secs.; weak glues, 26–27 secs.

Tensile strength of glue. Many methods have been suggested such as Bauschinger's, Kissling's, and Rideal's. Rideal has devised the following method:—

Two plane surfaces of biscuit porcelain, ground so as to fit, 1 square inch in area, are soaked with a solution made up of 1 part of glue in 2 parts of water at 70° for 30 minutes: they are placed together, weighted with 5 lbs., and kept for 5 days in a cool room. They are then fixed in a testing machine, and the weight necessary to tear them asunder is determined.

The writer has used with success a slightly modified form of a method originally suggested by Millar (J. Soc. Chem. Ind. 1899, 16). 10 p.c. solutions of the glues to be tested are made up. Strips of filter or other paper are cut, one inch in width and about 18 inches in length. These are dipped in the solution at about 50°, and then hung up to dry. When the first coat has dried, they are again immersed in the solution and allowed to dry, the portion that was lowest being placed at the top, so that as far as possible a uniform layer of glue is produced on their surfaces. After air drying, the strips are heated for 1 hour in the water-oven. Two or three lengths of 3 inches are cut out of the central portion of the strips. These are then separately tested by fixing between two indiarubber-covered clamps, one of which is fixed to the table and the other attached to the beam of a strong balance, the balance with the clamp, of course, being first counterpoised. Weights are added to the other pan until the paper breaks. A blank test is then made with the unsized paper, and this is deducted. Several experiments should be made, and the mean taken. A good glue should require some 9 or 10 lbs. when tested in this way to break the sized paper.

Foam test. Trotman and Hackford (J. Soc. Chem. Ind. 1906, 104) recommend the following procedure: A graduated tube, 70 cm. in length and of such a diameter that each 1 cm. in length has a capacity of 1 c.c., is half filled with a 10 p.c. solution of glue and placed in a water-bath. The temperature of the bath is maintained as nearly as possible at 60°. The tube is then corked, vigorously shaken for 1 min., and the top of the foam layer read off. The line of demarcation between the lower level of the foam and the liquid is too undefined to allow of reading, but that of the upper layer is constant. The peptones present in glue increase its tendency to foam.

The test is of importance for certain uses of glue, such as its application in veneering.

General remarks on the testing of glue.—Of course in each case, as already stated, the tests applied should refer directly to the uses to which the glue is to be put. For veneering and general joiner's work, for bookbinding and the like, a glue should have good tensile strength, little foaming power and good keeping qualities. It should also show a good jelly test and be free from grease, or it may give uneven joints. The glue for use in the sizing of canvas and the like should show a good strength of jelly and good tensile strength: foaming power and grease are of less importance. For the preparation of distempers, the grease content should be low, as it may give rise to 'flecks'; the keeping power should be high, but the tensile strength and strength of jelly are of less importance.

Hy. I.

GLUTAMIC ACID, *α-Aminoglutaric acid*

$CO_2H{\cdot}CH(NH_2)CH_2{\cdot}CH_2{\cdot}CO_2H$

was discovered by Ritthausen in 1866 (J. pr. Chem. [1] 99, 6, 454) among the products of the hydrolysis of wheat gluten by sulphuric acid, and hence called by him *glutaminic acid*. Subsequently, Ritthausen and Kreusler (J. pr. Chem. 1871, [2] 3, 214), Gorup-Besanez (Ber. 1877, 10, 780), Schulze (Zeitsch. physiol. Chem. 1892, 9, 253), and Wroblewski (Ber. 1898, 31, 3218) showed that it was formed by the hydrolysis of other vegetable proteids; and Hlasiwetz and Habermann (J. pr. Chem. 1873, [2] 7, 397), Panzer (Zeitsch. physiol. Chem. 1897, 24, 138), Abderhalden and Fuchs (*ibid.* 1908, 57, 339) isolated it from the products of hydrolysis of animal proteids. Osborne and Gilbert (Amer. J. Physiol. 1906, 15, 333) showed that the yield of glutamic acid from animal proteid matter varies from 7 to 10 p.c., whilst in vegetable proteids (with the exception of leucosine of wheat, 5·7 p.c.), the yield is larger, 12 to 37 p.c. A fruitful source of glutamic acid is beet-root molasses; Habermann (Annalen, 1875, 179, 248; Scheibler, Ber. 1884, 17, 1725; Andrlík, Zeitsch. Zuckerind. Böhm, 1903, 27, 665) obtained it to the extent of 7 p.c. on the dry solids of the molasses lye.

Kutscher (Zeitsch. physiol. Chem. 1899, 28, 123) isolated glutamic acid from the products of hydrolysis of casein by sulphuric acid, by precipitating the larger part of the organic bases with phosphotungstic acid, and removing the excess of sulphuric and phosphotungstic acids from the filtrate by means of barium hydroxide; the leucine and tyrosine crystallised out of the filtrate, and from the mother liquor the aspartic and glutamic acids were separated by the difference in solubility of their copper salts.

Glutamic acid contains an asymmetric carbon atom, and the dextro- and lævo-rotatory and the racemic variety of the acid are all known.

***d*-Glutamic acid**, the naturally occurring compound, crystallises in the rhombic system $a:b:c=0{\cdot}6868:1:0{\cdot}8548$ (Oebbeke, Ber. 1884, 17, 1725); m.p. 208° (213° corr.) with decomposition (Fischer, Ber. 1889, 32, 2451); is sparingly soluble in water, insoluble in alcohol or ether. It is dextro-rotatory in aqueous solution, $[\alpha]_D^{20°}+12{\cdot}04$; increasing amounts of strong acid cause a continuous increase of the specific rotation, which tends towards a maximum. The addition of bases first changes the dextro- into lævo-rotation, which attains its highest numerical value with the formation of the acid salt, further quantities of base convert the laevo-rotation again into a dextro-rotation. With lead hydroxide, no change in sign of the rotation takes place (Andrlík, Zeitsch. verein. deut. Zuckerind. 1903, 572, 948).

When glutamic acid is administered as a food, 96 p.c. is absorbed, a portion being used up in proteid synthesis, and the rest oxidised to urea (Andrlík and Velich, Zeitsch. Zuckerind. Böhm, 1908, 32, 313).

Glutamic acid is decomposed by the action of bacteria, yielding *n*-butyric acid, together with small quantities of succinic and formic acids (Brasch and Neuberg, Biochem. Zeitsch. 1908, 13, 299). When oxidised by hydrogen peroxide, it yields succinic acid (Dakin, J. Biol. Chem. 1909, 5, 409); and yields γ-hydroxyglutaric acid (glutanic acid, *q.v.*), when treated with nitrous acid (Ritthausen, J. pr. Chem. [1] 103, 239).

Glutamic acid forms normal and acid salts, the latter being the more general. Of these, the *sodium* $C_5H_8O_4NNa$, *potassium* $C_5H_8O_4NK$, *calcium* $(C_5H_8O_4N)_2Ca$, *barium* $(C_5H_8O_4N)_2Ba$, *lead* $(C_5H_8O_4N)_2Pb$, are crystalline and hygroscopic. The normal *ammonium salt*

$(NH_4)_2C_5H_7O_4N$

loses NH_3 at 110°-115°, and forms the *acid salt* $(NH_4)C_5H_8O_4N$; the *copper salt*

$C_5H_7O_4NCu,\frac{1}{2}H_2O$

is amorphous and greenish-blue, and dissolves in 400 parts boiling water (Wolff, Annalen, 1890, 260, 79); the *silver salts* $C_5H_7O_4NAg_2$ and $C_5H_8O_4NAg$ are white insoluble powders; and the *zinc salt* is basic $(C_5H_8O_4N)_2Zn,ZnO$ (Habermann, Annalen, 1871, 179, 248; Abderhalden and Kautzsch, Zeitsch. physiol. Chem. 1910, 64, 447; 68, 487). The *ethyl ester*

$C_5H_8(C_2H_5)O_4N$

is crystalline, and melts at 188° (Menozzi and Appiani, Gazz. chim. ital. 1894, 24, i. 384); the *diethyl ester* has b.p. 139°-140°/10 mm., sp.gr. 1·0737 at 17°, and $[\alpha]_D^{20°}+7{\cdot}34$ (Fischer, Sitzungsber. Akad. Wiss. Berlin, 1900, 48, 1062).

Glutamic acid forms a soluble benzene sulphonyl derivative, $SO_2Ph{\cdot}NH(C_3H_5)(CO_2H)_2$ (Hedin, Ber. 1890, 23, 3196); and the following *acyl* derivatives are described by Fischer (Ber. 1907, 40, 3704), Fischer, Kropp and Stahlschmidt (Annalen, 1909, 365, 181): *l-leucyl-d-glutamic acid*

$CHMe_2{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CO{\cdot}NH{\cdot}CH(CO_2H){\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H$,

m.p. 232° (decomp. corr.), has $[\alpha]_D^{20°}+10{\cdot}5°$ in N/1-HCl, forms soluble sodium and barium salts, the silver salt being sparingly soluble; *chloracetyl-d-glutamic acid*

$CH_2Cl{\cdot}CO{\cdot}NH{\cdot}CH(CO_2H){\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H$,

m.p. 143° (corr.), $[\alpha]_D^{20°}-13{\cdot}5°$ ($\pm 0{\cdot}2°$) in aqueous solution, yields *glycyl-d-glutamic acid*

$NH_2{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}CH(CO_2H)[CH_2]_2CO_2H$,

m.p. 178° (corr.), $[\alpha]_D^{20°}-6{\cdot}3°$; *chloracetylglutamyldiglycinediethyl ester*

$CH_2Cl{\cdot}CO{\cdot}NH{\cdot}CH\langle{}^{CO{\cdot}NH{\cdot}CH_2{\cdot}CO_2Et}_{CH_2{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}CO_2Et}$

m.p. 146° (corr.), yields on hydrolysis *chloracetylglutamyldiglycine* $C_{11}H_{16}O_7N_3Cl$, m.p. 173° (decomp. corr.), and yields on treatment with aqueous ammonia *glycylglutamyldiglycine* $C_{11}H_{18}O_7N_4$, m.p. 248° (corr.).

***r*-Glutamic acid** has been synthesised by Wolff (Annalen, 1890, 260, 79) from lævulic acid. Glyoxylpropionic acid

$OHC{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H$

obtained by boiling dibromolævulic acid with water, reacts with hydroxylamine to form γδ-di*iso*nitrosovaleric acid

$CH(NOH)C(NOH)CH_2{\cdot}CH_2{\cdot}CO_2H$,

from which *iso*nitrosocyanobutyric acid

$CN{\cdot}C(NOH){\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H$

is obtained by hydrolysis with sulphuric acid and subsequent treatment with cold sodium hydroxide. When *iso*nitrosocyanobutyric acid

is hydrolysed with boiling alkali, it yields *iso*-nitrosoglutaric acid

$$CO_2H{\cdot}C(NOH){\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H,$$

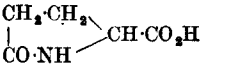
and this is reduced to inactive glutamic acid

$$CO_2H{\cdot}CH(NH_2)CH_2{\cdot}CH_2{\cdot}CO_2H$$

by tin and hydrochloric acid. *r*-Glutamic acid can be prepared from the dextro- isomeride by heating it with barium hydroxide (Schulze and Bosshard, Ber. 1885, 18, 388; Schulze, Zeitsch. physiol. Chem. 1892, 9, 253).

r-Glutamic acid crystallises from hot water in rhombic plates, $a:b:c=0{\cdot}7454:1:1{\cdot}2367$, m.p. 199° (decomp. corr.), dissolves in 66·7 parts water at 20°, and is sparingly soluble in ether, alcohol, carbon disulphide, or light petroleum. The *copper salt* $C_5H_7O_4NCu,2\frac{1}{2}H_2O$ forms blue needles, becomes anhydrous at 135°, and is not soluble in less than 1000 parts of boiling water. The *hydrochloride* crystallises in needles, m.p. 193° (decomp.) (Wolff), 200° (Abderhalden and Kautzsch, Zeitsch. physiol. Chem. 1910, 68, 487), and is crystallographically identical with the hydrochloride of the *d*-acid, $a:b:c=0{\cdot}8873:1:0{\cdot}3865$ (Wolff, *l.c.*).

When *r*-glutamic acid is heated at its melting-point, it decomposes, yielding *pyrrolidonecarboxylic acid*



This compound has m.p. 182°–183°, and is identical with the pyroglutamic acid obtained by Haitinger (Monatsh. 3, 228) by heating *d*-glutamic acid, and also with the glutimic acid of Schutzenberger (Ann. Chim. Phys. [5] 16, 372), obtained by decomposing albumin with barium hydroxide at 180° (compare also Abderhalden and Kautzsch, Zeitsch. physiol. Chem. 1910, 68, 487). *r-Benzoylglutamic acid* crystallises with $1H_2O$, m.p. 152°–153° (155°–157° corr.), and is soluble in 124 parts of water at 20° (Fischer, Ber. 1899, 32, 2451). *Chloracetyl-r-glutamic acid* has m.p. 123°; *glycyl-r-glutamic acid* is a hygroscopic powder, and forms a *copper salt* crystallising with $3\frac{1}{2}H_2O$ that decomposes at 223° (corr.) (Fischer, Kropp and Stahlschmidt, Annalen, 1909, 365, 181).

l-Glutamic acid. When *r*-glutamic acid is crystallised form water, right- and left-handed enantiomorphous crystals are deposited, but this fact cannot conveniently be utilised for the preparation of the *l*-isomeride; this was, however, effected by the cultivation of *Penicillium glaucum* in a solution of the *r*-acid, whereby the *d*-acid is destroyed and the *l*-acid remains in solution (Menozzi and Appiani, Gazz. chim. ital. 1894, 24, i. 370). Fischer (Ber. 1899, 32, 2451) resolved *r*-benzoylglutamic acid by the fractional crystallisation of the strychnine salt; *benzoyl-l-glutamic acid* has m.p. 130°–132° (corr.), dissolves in less than two parts of water at 100°, or 21 parts at 20°, and has $[\alpha]_D+13{\cdot}81°$ in 5 p.c. aqueous solution, and the potassium salt has $[\alpha]_D-18{\cdot}7°$; it yields *l-glutamic acid* on hydrolysis, and this is identical with the *d*-isomeride, except that its hydrochloride has $[\alpha]_D^{20°}-30{\cdot}05°$, whilst that of the *d*-acid is $+30{\cdot}45°$.

l-Pyrrolidonecarboxylic acid, obtained by heating *d*-glutamic acid at 150°–160°, forms large colourless orthorhombic crystals, m.p. 162°, $a:b:c=1{\cdot}5034:1:1{\cdot}6292$, and has $[\alpha]_D$ $-11{\cdot}5°$ (Menozzi and Appiani, Gazz. chim. ital. 1894, 24, i. 370; Abderhalden and Kautzsch, Zeitsch. physiol. Chem. 1910, 68, 487). M. A. W.

GLUTAMINE $CO_2H{\cdot}C_3H_5(NH_2)CONH_2$ is the half amide of glutamic acid. It was discovered in 1877 by Schulze and Urich (Ber. 10, 85) in the juice of young pumpkin plants, and isolated from beet-root sap by Schulze and Bosshard (*ibid.* 1883, 16, 312), one litre yielding 0·7 to 0·9 gram of glutamine. It appears to replace its homologue asparagine in some natural orders, *e.g. Carophyllaceæ*, *Cruciferæ*, and *Filices*, where it occurs in the leaves, seedlings, roots, and tubers. The greatest amount of glutamine found in seedlings is only 2·5 p.c. of the dry matter which is much less than the amount of asparagine found in leguminous seedlings, but it is probable that, owing to the difficulties of separating glutamine, the plant contains at least twice as much as is actually isolated (Schulze, Zeitsch. physiol. Chem. 1894, 20, 327; 1897, 24, 18; Ber. 1896, 29, 1882; Landw. Versuchs.-Stat. 1898, 49, 442). Glutamine occurs with asparagine in the juice of ripening oranges (Scurti and De Plato, Chem. Zentr. 1908, ii. 16, 1370).

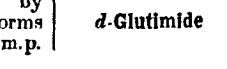
Glutamine crystallises in needles; it dissolves in about 25·7 parts of water at 16° (Schulze and Godet, Landw. Versuchs.-Stat. 1907, 67, 313), and is sparingly soluble in alcohol. It behaves as a very weak acid towards indicators (Sellier, Chem. Zentr. 1904, i. 789). Glutamine is dextro-rotatory in aqueous solution, seven specimens from various vegetable sources were found to have $[\alpha]_D$ between $+1{\cdot}9°$ and $+9{\cdot}5°$, the differences being probably due to the presence of the two stereoisomerides in varying proportions (Schulze and Bosshard, Ber. 1885, 18, 390; Sellier, Chem. Zentr. 1904, i. 789; Schulze, Ber. 1906, 39, 2932; Landw. Versuchs.-Stat. 1906, 65, 237).

The estimation of glutamine is best effected by Schlösing's method (Schulze, J. pr. Chem. 1885, [2] 31, 233), as the $-CO{\cdot}NH_2$ group is completely hydrolysed when distilled with magnesia under the ordinary pressure, but if the pressure be reduced sufficiently to cause the solution to boil at 40°, hydrolysis does not take place, and under these conditions ammonium salts may be completely removed (Sellier, Bull. Soc. chim. Sucr. Dist. 1907, 25, 124; Schulze, Landw. Versuchs.-Stat. 1906, 65, 237).

Owing to the feebly acidic character of glutamine, very few salts have been isolated: the *copper* derivative, $Cu(C_5H_9O_3N_2)_2$, forms bluish violet crystals, the *cadmium* derivative, $Cd(C_5H_9O_3N_2)_2$, forms fine prisms; and is decomposed by boiling water. Glutamine forms a *compound* with tartaric acid, that separates in large transparent crystals (Schulze and Godet, Landw. Versuchs.-Stat. 1907, 67, 313).

By the action of alcoholic ammonia on the ester of *d*- or *l*-glutamic acid, the amide of the corresponding pyrrolidonecarboxylic acid is formed; these are called *glutimides* by Menozzi and Appiani, and the dextro- and lævo-rotatory and the racemic variety are described.

***d*-Glutimide**



crystallises in needles belonging to the anorthic system, $a:b:c=1{\cdot}403:1:1{\cdot}421$, $\beta=86{\cdot}55°$; it has m.p. 165°, and $[\alpha]_D+41{\cdot}29°$. *l-Glutimide* has $[\alpha]_D-40°$, and has the same melting-point and other properties as its dextro-isomeride. *r*-Glutimide is formed when *l*-glutimide is heated with alcoholic ammonia at 140°–150°, or alone at 200°; it has m.p. 214°, and crystallises in the orthorhombic system, $a:b:c=0{\cdot}8853:1:0{\cdot}3866$ (Menozzi and Appiani, Atti. R. Accad. Linc. 7, i. 33; Gazz. chim. ital. 1894, 24, i. 370).

M. A. W.

GLUTANIC ACID, *α-hydroxyglutaric acid*, is formed when nitrous acid reacts with glutamic acid (Markownikoff, Annalen, 1876, 182, 347); it occurs in molasses, and was isolated in the form of the zinc salt from the ethereal extract of the product of the action of dilute nitric acid at 70° on casein (Habermann and Ehrenfeld, Zeitsch. physiol. chem. 1902, 35, 231). The *zinc salt* $C_5H_6O_5Zn,3H_2O$ and the *magnesium salt* $C_5H_6O_5Mg,4H_2O$ are well defined (Markownikoff, *l.c.*). The free acid has not been isolated, but forms *butyrolactone-γ-carboxylic acid* $\begin{matrix}CH_2\cdot CH_2\\ |\\ CO—O—\end{matrix}\!\!>\!CH\cdot CO_2H$, m.p. 49°–50°, when an aqueous solution is evaporated at 100°, and the resulting syrup allowed to crystallise over sulphuric acid.

Ethylbutyrolactonecarboxylate

$$\begin{matrix}CH_2\cdot CH_2\\ |\\ CO—O—\end{matrix}\!\!>\!CH\cdot CO_2Et.$$

prepared by the action of epichlorhydrin on ethylsodiomalonate, is a colourless oil, b.p. 175°/25 mm. (Traube and Lehmann, Ber. 1901, 34, 1971).

M. A. W.

GLUTARIC ACID $C_5H_8O_4$. Glutaric acid and its alkyl derivatives, when heated, break down into anhydrides and water. The anhydrides readily yield anilic acids, from which anils can be obtained by the withdrawal of water (Auwers, Oswald, and Thorpe, Annalen, 285, 229). The glutaric acids resemble the succinic acids in their reactions, but they are not so volatile in steam, and not so readily changed to anhydrides by acetylchloride.

Glutaric acid. Normal pyrotartaric acid

$$CO_2H[CH_2]_3CO_2H.$$

Found in Caucasian naphtha (Markownikow, Ber. 1897, 947), in beet-root (Lippmann, *ibid.* 1891, 3299), and in the wash-water from raw sheep wool. Prepared by oxidising fats (Bouveault, Bull. Soc. chim. 19, [3] 562), stearic and oleic acids (Carette, *ibid.* 46, 65) or sebacic acid (Carette, *ibid.* 45, 270), with nitric acid; by treating 1:3-dicyanopropane with hydrochloric acid (Reboul, Ann. Chim. Phys. 14, [5] 14, 501; Markownikow, Annalen, 182, 341); by treating β-hydroxyglutaric acid with hydriodic acid at 180° (Pechmann and Jenisch, Ber. 1891, 3252); by the action of baryta on ethyl pentanehexacarboxylate (Bottomley and Perkin, Chem. Soc. Trans. 1900, 300); by treating ethyl malonate with methylene chloride, hydrolysing the product with caustic potash and heating the dicarboxylglutaric acid thus formed to 200° (Conrad and Guthzeit, Annalen, 222, 257; Perkin, Ber. 1886, 1055); by condensing ethylsodiomalonate with formaldehyde in the presence of a small quantity of piperidine or diethylamine, and heating the methylene dimalonic acid thus formed with hydrochloric acid (Knoevenagel, Ber. 1894, 2346); by the electrolysis of equal quantities of the potassium salts of the methyl hydrogen succinate and malonate (Vanzetti and Coppadro, Chem. Zentr. 1904, i. 1254; 1903, ii. 1053); by treating hydroresorcin with sodium hypobromite (Vörlander and Kohlmann, Ber. 1899, 1878); by treating cyclopentanone with nitric acid (Wislicenus, Annalen, 275, 318) or with acetic anhydride, and subsequently with potassium permanganate (Mannich and Hancu, Ber. 1908, 572); by the action of nitric acid on methylcyclopentane (Markownikow, *ibid.* 1900, 1908), or on cyclopentane (Markownikow, *ibid.* 1897, 975); by treating α-acetoglutaric ester with concentrated potash (Vörlander and Knötzsch, Annalen, 294, 318; Wislicenus and Limpach, *ibid.* 192, 128); by treating glutaconic acid with sodium amalgam (Conrad and Guthzeit, *ibid.* 222, 254); by the oxidation of piperidine with hydrogen peroxide (Wolffenstein, Ber. 1892, 2777).

Glutaric acid crystallises in large monoclinic plates, m.p. 97·5°; 100 c.c. of water dissolve 42·9 parts of acid at 0°, 63·9 at 20°, and 95·7 at 50° (Lamouroux, Compt. rend. 128, 998); readily soluble in alcohol and ether. It condenses with aldehydes to form substituted glutaric acids (Fittig and Roedel, Annalen, 282, 334, 338, 344; Knoevenagel, Ber. 1894, 2346): electrolysis of the potassium salt of the monoethyl ester gives rise to the diethyl ester of suberic acid (Brown and Walker, Annalen, 261, 119). By heating glutaric acid at 230°–280°, or by treating the silver salt with acetyl chloride, *glutaric anhydride*, m.p. 56°–57°, is produced (Fichter and Herbrand, Ber. 1896, 1193). When treated with aluminium amalgam, the anhydride is converted into a mixture of glutaric and δ-hydroxyvaleric acids, the latter of which readily changes into δ-hydroxyvalerolactone (Fichter and Beisswenger, Ber. 1903, 1200).

The *dimethyl ester of glutaric acid* is a colourless liquid, b.p. 213·5°–214° (751 mm.), sp.gr. 1·09337 15°/4° (Meerburg, Rec. trav. chim. 1899, 367); the *diethyl ester* boils at 236·5°–237° (corr.), and has sp.gr. 1·0284 at 15° (Perkin, Chem. Soc. Trans. 1888, 567).

The three possible isomerides of glutatic acid are all known and are described below.

Pyrotartaric acid. Methylsuccinic acid (Ger. *Brenzweinsaüre*; *Methylbernsteinsaüre*)

$$CO_2H\cdot CH(CH_3)\cdot CH_2\cdot CO_2H.$$

Obtained from suint (Buisine, Compt. rend. 107, 789). Prepared by the dry distillation of tartaric, racemic, or pyruvic acids (Fourcroy and Vanquelin, Ann. Chim. Phys. 35, (i.) 161; 64, 42; Wolff, Annalen, 317, 22; Béchamp, Zeitsch. Chem. 1870, 371; Bourgoin, Ann. Chim. Phys. 12, [5] 419; by heating pyruvic acid with hydrochloric acid (Wolff, *l.c.*; Jong, Rec. trav. chim. 21, 191); by the reduction of citra-, ita-, or mesaconic acids with sodium amalgam (Kekulé, Annalen, Spl. 1, 338; Spl. 2, 95); by the reduction of the anhydride of citraconic acid with hydrogen in the presence of nickel, when pyrotartaric acid and its anhydride

are produced (Eijkman, Chem. Zentr. 1907, i. 1617); by treating β-cyanobutyric acid with caustic potash (Wislicenus, Annalen, 165, 93; Bredt and Kallen, *ibid.* 293, 350); by fusing gamboge with caustic alkali (Hlasiwetz and Barth, *ibid.* 138, 73); by treating aldehydo*iso*butyric acid with nitric acid (Perkin and Spranklin, Chem. Soc. Trans. 1899, 19; Bischoff and Kuhlberg, Ber. 1890, 634); by the interaction of ethylsodiomalonate with ethylbrompropionate and subsequent boiling with hydrochloric acid (Bone and Sprankling, Chem. Soc. Trans. 1899, 848); by the interaction of ethylsodiomethylmalonate and ethylchloracetate or of ethylsodioethenyltricarboxylate and methyliodide, and subsequently hydrolysing the ester of methylethenyltricarboxylic acid thus formed (Bischoff and Kuhlberg, *l.c.*); by treating ethyldibromomethylacetoacetate with concentrated potash and subsequently with sulphuric acid (Cloez, Compt. rend. 110, 583); by treating calcium lactate with potassium permanganate, when calcium pyrotartrate is produced (Wiegand, Ber. 1884, 840).

Pyrotartaric acid crystallises in triclinic prisms, m.p. 117°-118° (Ladenburg), 112° (Perkin). Soluble in water, alcohol, and ether. By heating pyrotartaric acid with dilute sulphuric acid at 150°, acetaldehyde and formic acid are produced (Wiegand, *l.c.*); by condensation with acetaldehyde, benzaldehyde, &c., substituted paraconic acids are produced (Fittig, Annalen, 255; 108, 126, 257); with salicaldehyde, coumarinpropionic acid is produced (Fittig and Brown, *ibid.* 255, 285). Methylthiophen is produced by the distillation of the sodium salt with phosphorus pentasulphide. Pyrotartaric acid contains an asymmetric carbon atom, and it has been resolved into its two optically active antipodes by means of the fractional crystallisation of its strychnine salt (Ladenburg, Ber. 1895, 1170; 1896, 1254; Annalen, 364, 227).

Pyrotartaric anhydride is obtained by heating the acid above 200°, or by treating the acid with acetylchloride (Perkin, Chem. Soc. Trans. 1888, 564; Fichter and Herbrand, Ber. 1896, 1193); m.p. 31·5°-32°; b.p. 247·4° (corr.), sp.gr. 15°/15°, 1·2378. By reduction with hydrogen in the presence of nickel, the anhydride yields butyrolactone (Eijkman, Chem. Zentr. 1907, i. 1617), and with sodium amalgam and hydrochloric acid, α-methylbutyrolactone (Fichter and Herbrand, *l.c.*).

The *dimethyl ester* of *pyrotartaric acid* is a colourless oil, b.p. 197°; and the *diethyl ester* boils at 217·5-218·5°.

Dimethylmalonic acid, β-Isopyrotartaric acid $(CH_3)_2C(CO_2H)_2$. Obtained by the oxidation of fenchone with nitric acid (Gardner and Cockburn, Chem. Soc. Trans. 1898, 708); by the oxidation of phoronic acid with nitric acid or with potassium permanganate in alkaline solution (Pinner, Ber. 1882, 585; Anschütz, *ibid.* 1893, 827; Anschütz and Walter, Annalen, 368, 95); by the oxidation of filicinic acid, obtained from filicin, which is extracted from *Filix mas* (male fern) (Boehm, Chem. Zentr. 1896, ii. 1036; Daccomo, Gazz. chim. ital. 24, 1, 517); by the oxidation of camphor with nitric acid (Bredt, Ber. 1894. 2093). Prepared by treating α-cyan*i*obutyric acid with hydrochloric acid (Markownikow, Annalen, 182, 336); by heating 5: 5-dimethylbarbituric acid with caustic potash (Conrad and Guthzeit, Ber. 1881, 1644); by the oxidation of αα-dimethylglutaconic acid with potassium permanganate (Henrich, Ber. 1899, 670; Perkin, Chem. Soc. Trans. 1902, 255).

Dimethylmalonic acid is best obtained pure from its zinc salt; m.p. 190° (Perkin, Chem. Soc. Trans. 1903, 1237), 192°-193° (Königs and Hörlin, Ber. 1893, 2049); sparingly soluble in water and alcohol, readily soluble in ether; decomposes on heating into carbon dioxide and *iso*butyric acid. Dimethylmalonylchloride yields a duodecimolecular anhydride on treatment with aqueous pyridine: it is an amorphous white powder, m.p. 145°-148° (Einhorn, Annalen, 359, 169). *Dimethylmalononitrile* is prepared by treating dimethylcyanacetamide with phosphoric oxide or phosphorus pentachloride (Hesse, Annalen, 18, 723; Errera and Berti, Gazz. chim. ital. 26, ii. 224), m.p. 32°, b.p. 162·5°. *Dimethylmalonamide* is prepared from the methyl ester and concentrated aqueous ammonia (Perkin, Chem. Soc. Trans. 1903, 1242; Thorne, *ibid.* 1881, 545); from the ethyl ester and alcoholic ammonia (Fischer and Dilthey, Ber. 1902, 851, 855); from dimethylmalonylchloride and concentrated aqueous ammonia (Meyer, Ber. 1906, 198), m.p. 269° (corr.) (Perkin). The *dimethyl ester* is a colourless liquid, b.p. 177°-178° (753 mm.); the *diethyl ester* boils at 194·5°. The latter may be obtained by treating the ester of dimethylcyanacetic acid with sulphuric acid: on treatment with alkali and urea, dimethylbarbituric acid is obtained (Merck, Chem. Zentr. 1905, ii. 1141; D. R. P. 163200). The diethyl ester of dimethylmalonic acid condenses with brom*iso*butyric ester in the presence of zinc to form the ester of tetramethylacetonedicarboxylic acid (Shdanowitsch, Chem. Zentr. 1907, i. 519). The potassium salt of the monoethyl ester is converted by electrolysis into the diethyl ester of tetramethylsuccinic acid (Brown and Walker, Annalen, 274, 48).

Ethylmalonic acid. Isopyrotartaric acid $CH_3{\cdot}CH_2{\cdot}CH(CO_2H)_2$.

Prepared by boiling the ethyl ester of α-cyanobutyric acid with potash (Wislicenus and Urech, Annalen, 165, 93; Tupolew, *ibid.* 171, 243; Markownikow, *ibid.* 182, 329); the diethyl ester is produced by treating ethyl malonate with sodium or zinc and ethyl iodide (Daimler, *ibid.* 249, 174; Schukowsky, Chem. Soc. Abstr. 1888, 1179; Schey, Rec. trav. chim. 16, 356; Michael, J. pr. Chem. 72, [2] 537). Crystallises in rhombic prisms, m.p. 111·5°; readily soluble in water, alcohol, and ether; decomposes on heating into butyric acid and carbon dioxide.

Ethylmalononitrile is prepared from ethylcyanacetamide and phosphorus pentachloride; it is a colourless oil, b.p. 200° (Hessler, Annalen, 1899, 169; Henry, J. 1889, 637). *Ethylmalonamide* is prepared by the action of sodium ethoxide and ethyliodide on malonamide (Meyer, Monatsh. 28, 1; Conrad and Schulze, Ber. 1909, 730); by treating the diethyl ester with concentrated aqueous ammonia (Freund and Goldsmith, *ibid.* 1888, 1245); m.p. 214°. The *diethyl ester* boils at 207°; when the sodium derivative of this ester is condensed with ethylbrommalonate in alcoholic solution, the

ethyl ester of ethylenetetracarboxylic acid is produced (Bischoff, Ber. 1896, 1514).

GLUTEN. Wheaten flour differs from that of all other cereals in that after it has been made into a dough with a little water, it is possible to wash out the starch, leaving a sticky adhesive brown or greyish-brown residue which consists mainly of protein. This is crude gluten: on drying it in a water-oven, a hard brittle horny mass, not unlike glue, results, which has lost its power of becoming plastic when wetted, and strongly adheres to the substance on which it rests. At a higher temperature, the wet gluten expands greatly until the expansive force ruptures its vesicles.

The flour of other cereals when washed in a similar way entirely disintegrates, leaving no protein residue. The physical properties of wheaten dough depend almost entirely on the gluten, which acts as a mechanical agency for binding the particles of starch and for entangling the carbon dioxide gas produced by the fermentation: in the oven, this gas expands, causing the dough to rise and the gluten to remain distended until the heat fixes it.

Crude gluten varies in colour from grey to brown. Besides protein, it contains traces of starch, fibre, cholesterol, fat, and a small proportion of mineral matter. It is insoluble in tap water, strong alcohol, and ether, but dissolves partly in distilled water, in dilute alkalis and more slowly in dilute acids.

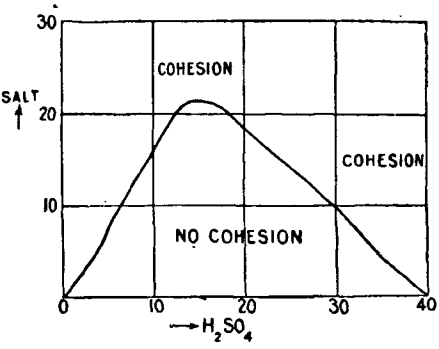
Gluten, after treatment with dilute acids or salts, has some diastatic action, which the freshly prepared gluten lacks (Reychler, Ber. 1889, 22, 414; *see also* Baker, J. Soc. Chem. Ind. 1908, 27).

The quantity of gluten in wheaten flour varies considerably according to its race and the country in which it was grown. Further, the best patent flour, milled from the centre of the grain, contains slightly less gluten than the households flour from the outer layers of the same grain.

Speaking very generally, the proportion of gluten varies from 8 to 15 p.c., though exceptional flours may have either less or more than this amount. English flours as a class have about 10 p.c. or less gluten, Canadian and American spring wheat flours, *e.g.* the so-called No. 1 Manitoba, contain 13 p.c. and upwards. The strength of a flour depends, however, not so much on the quantity of gluten present as on its quality. A gluten, though present in satisfactory quantity, may be too tough, or hard and brittle, or it may be too elastic and have no power of retaining the gas in its pores.

Gluten consists mainly of two proteins, *gliadin* and *glutenin*, both of which are essential for its formation. The gliadin forms a sticky network which entangles the glutenin to make a compact mass. The presence of soluble salts, *i.e.* electrolytes, is also essential, but the mineral constituents of the flour are sufficient for this purpose. In distilled water, gluten partly dissolves, the semi-fluid residue having no tenacity. Pure gluten has of itself neither ductility nor tenacity, and the physical properties like those of other colloidal substances depend upon the electrolytes present in the dough.

The researches of Wood and Hardy (Wood, J. Agric. Sci. 1907, 2, 139, 267; Wood and Hardy, Proc. Roy. Soc. 1909, B, 81, 38; Summary by Hardy, Brit. Assoc. Report, Winnipeg, 1909) have shown that any salt confers cohesion upon gluten; any acid or alkali, when sufficiently dilute, lessens or destroys it. Gluten which has lost cohesion owing to the action of an acid, may be rendered coherent again by the addition of salt. There is a definite relation between the concentration of the acid and the amount of salt required to undo its action. As the concentration of the acid is increased, the amount of salt needed to maintain cohesion rises to a maximum, and thence falls until a point is reached when the acid alone is sufficient. The curve shows the



concentration of salt and acid needed just to preserve cohesion: it encloses an area of no cohesion, whilst outside it is a region of cohesion. The areas represent continuous changes as is characteristic of colloidal matter: a line inclined upwards follows a system in which there is continual separation of water and gluten; in consequence the water-holding power of the protein becomes less and less, the tenacity grows, and the ductility diminishes.

In practice, the water-holding capacity, or *hydration ratio*, of gluten is of considerable significance. It is measured by the ratio of the wet gluten immediately after extraction under carefully standardised conditions to its weight after drying. On the average, it is about 3 : 1; that is, gluten carries about twice its weight of water. It varies from 2·5 in strong flours to above 3 in very weak flours.

The ratio of gliadin to glutenin in different wheats is not constant. It appears to be about 50 p.c. According to Shutt (J. Soc. Chem. Ind. 1909, 28, 336), there is a relationship between the maturity of the grain and the gliadin content, the more fully ripened wheat containing the higher proportion.

Gluten may be estimated in flour as follows: 30 grams of flour are made into a dough with from 12 to 15 c.c. of water, and set aside for an hour. The dough is then worked between the fingers in a stream of running water to wash out the starch, being held over a muslin screen, so that any particles which are dropped can be recovered. Finally the gluten is worked vigorously between the fingers to remove the last traces of starch. With practice the washing can be carried out so as to occupy always the same time. The ball of gluten is then placed under water for an hour. It is next freed from

excess of moisture by working between the hands and wiping off excess of water until the moment when the ball begins to stick: it is then removed to a little square of parchment paper, weighed, and dried for at least 24 hours at 100°. The ratio of the wet and dry weights gives the hydration ratio. Considerable information as to the strength of the gluten is gained by the feel both of the dough and of the gluten between the fingers. The method, though empirical, gives with practice very trustworthy results.

It was at one time customary to test the quality of the gluten in an aluerometer. The wet gluten was placed in a tube provided with a piston, heated to a definite temperature (150°), and the amount of expansion read off. This test is of very little value.

As a check on the gluten estimation, the total nitrogen may be determined by Kjeldahl's method in the flour and in the crude dry gluten, and multiplied by 5·7 to express it as protein.

Gluten in the form of a light-brown powder, dried at a low temperature, is a commercial product, being used for the manufacture of bread and biscuits for diabetic patients: it usually contains from 3 to 5 p.c. of starch, and sometimes a great deal more, and should yield a very tough elastic dough when wetted.

Westrup (Eng. Pat. 4028, 1908; 8337, 1909) proposes to test the strength of flours by making a ball of 15 grams flour and 7·5 grams of water, and placing this under a disc of plate glass, 3½ inches in diameter. A 200-gram weight is put on the glass for 30 minutes. The dough is pressed out, and, after hardening for 24 hours, the circumference of the flattened cake is measured by rolling it along a scale. Different flours are flattened to different extents.

Baine (Eng. Pat. 14770, 1909) puts a dough of standard proportions into a cylinder provided with a piston. As the dough rises, the piston is pushed up, an arresting mechanism prevents it dropping from the highest point reached, which can be read off later.

Neither of these methods appears to be of much practical value.

Gliadin. Wheat gluten was first separated into two constituents in 1819 by Taddei, who termed the alcohol soluble protein gliadin. Subsequently, Ritthausen thought gliadin to consist of three different proteins, but the researches of Osborne and others have made it clear that only one alcohol-soluble protein is present in wheat.

The alcohol-soluble protein of rye is apparently identical with that of wheat, and is therefore also termed gliadin. Other alcohol-soluble cereal proteins are the hordein of barley and zein of maize; these, however, are quite different from gliadin. Osborne has proposed to call this group *prolamins*.

The solubility of gliadin is a maximum in 70 p.c. ethyl alcohol—it is nearly insoluble in water and in absolute alcohol. When dehydrated with absolute alcohol and dried over sulphuric acid, gliadin is obtained as a colourless friable substance. As precipitated from dilute alcohol or water and dried, it is amorphous and transparent, somewhat resembling gelatin, but it is more brittle. It turns sticky with distilled water, and part dissolves, still more being dissolved on boiling. The addition of the smallest quantity of a mineral salt immediately precipitates it completely, either from aqueous or dilute alcoholic solution. The salts with acids or alkalis are freely soluble in water. They are precipitated unchanged on neutralisation.

Gliadin may be extracted both from gluten and from flour with 70 p.c. alcohol. The residue will no longer form a dough when wetted with water.

Gliadin has the composition C=52·72 p.c., H=6·86 p.c., N=17·66 p.c., S=1·03 p.c., O=21·73 p.c., and gives 5738 calories per gram on combustion (Benedict and Osborne, J. Biol. Chem. 1907, 3, 119). The specific rotation in 70 p.c. alcohol is −92° (Mathewson, J. Amer. Chem. Soc. 1906, 28, 1482): the same author has determined the rotatory power in a number of solvents.

The total nitrogen, 17·66 p.c., is distributed as follows: as ammonia 4·33 p.c., basic 1·09 p.c., non-basic 12·17 p.c

Osborne and Clapp (Amer. J. Physiol. 1906, 17, 231) have made a very careful determination of the products of hydrolysis of gliadin (*see also* Abderhalden and Samuely, Zeitsch. physiol. Chem. 1905, 44, 276). Their figures are as follows:—

	p.c.		p.c.
Glycine	absent	Tyrosine	1·20
Alanine	2·00	Cystine	0·45
Valine	0·21	Lysine	absent
Leucine	5·61	Histidine	0·61
Proline	7·06	Arginine	3·16
Phenylalanine	2·35	Ammonia	5·11
Aspartic acid	0·58	Tryptophan	present
Glutamic acid	37·33		
Serine	0·13	Total	65·80

The striking points in the composition are the absence of glycine and lysine and the small proportion of basic amino acids, the very large quantity of glutamic acid and the high proportion of ammonia and proline.

About 60 p.c. of the total sulphur in gliadin is converted into sulphide on boiling with sodium hydroxide.

Glutenin. The second protein of gluten is characterised by being insoluble in water, saline solutions, and alcohol, and remains after exhaustive treatment of gluten with these three solvents. When freshly prepared, it is soluble in 0·1 p.c. potassium hydroxide and 0·2 p.c. hydrochloric acid, and also in very dilute sodium carbonate and ammonia. After drying over sulphuric acid, it forms an amorphous greyish-brown powder somewhat less soluble in these reagents. It is precipitated on neutralisation. The only other cereal protein described, similar to glutein, is the oryzenin of rice (Rosenheim and Kajiura, J. Physiol. 1908, 36, liv.), although it is probable that other seeds contain similar proteins. Osborne groups these as *glutelins*.

Glutenin has the composition, C=52·34 p.c., H=6·83 p.c., N=17·49 p.c., S=1·08 p.c., O=22·26 p.c.; heat of combustion 5704 calories (Benedict and Osborne, J. Biol. Chem. 1907, 3, 119). The nitrogen is distributed as follows: ammonia, 3·30 p.c.; basic, 2·05 p.c.; non-basic, 11·95 p.c.

According to Osborne and Clapp, the products of hydrolysis are:

	p.c.		p.c.
Glycine	0·89	Tyrosine	4·25
Alanine	4·65	Cystine	0·02
Valine	0·24	Histidine	1·76
Leucine	5·95	Arginine	4·72
Proline	4·23	Lysine	1·92
Phenylalanine	1·97	Ammonia	4·01
Aspartic acid	0·91	Tryptophan	present
Glutamic acid	23·42		
Serine	0·74		59·68

[See the Discussion on Wheat, Brit. Assoc. Report, Winnipeg, 1909, Supplement to J. Board of Agric. 1910, vol. 17, No. 3; *see also* T. B. Osborne, Pflanzenproteine, Wiesbaden, 1910; Jago, Science and Art of Bread-making, London, 1911.] E. F. A.

GLUOTOL *v.* SYNTHETIC DRUGS.

GLYCERIN (*Glycerol, Glycyl alcohol, Propenyl alcohol* $C_3H_8O_3$ or $C_3H_5(OH)_3$) occurs in combination with fatty acids in all fatty oils and fats. Glycerin was discovered by Scheele, when preparing lead plaster from olive oil, and was termed by him '*principium dulce.*' The fatty oils and fats may be regarded as salts formed by the combination of fatty acids and glycerol, with the loss of three molecules of water. Glycerol being a trihydric alcohol, and consequently behaving like a trihydric base, is able to combine with three radicles of fatty acids, as is expressed by the following equation, in which R represents the acid radicle of any fatty acid:—

$$C_3H_5\begin{matrix}O\cdot H\\O\cdot H\\O\cdot H\end{matrix}+3R\cdot OH=C_3H_5\begin{matrix}O\cdot R\\O\cdot R\\O\cdot R\end{matrix}+3H_2O.$$

This equation, when read from right to left, symbolises the process of saponification of fats, and expresses the fact, that by the addition of water (under suitable conditions) to the neutral glycerides, the latter are resolved into three molecules of fatty acids and one molecule of glycerol (*see* SAPONIFICATION). From the right side of the equation it follows that glycerol does not exist as such in the fatty oils and fats, but that it is formed by the assimilation of three molecules of water. Hence the sum of the weight of the fatty acids and glycerol is always greater than the weight of the original fat employed. The excess over 100 p.c. may be gathered from the following table by adding up the numbers given in column 4, and deducting 100 from that sum (*see* column 5).

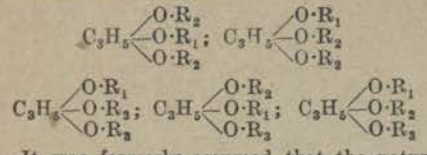
Owing to this complete analogy between the formation of a tribasic salt and a triglyceride, the natural triglycerides are also termed 'neutral glycyl esters.'

The triglycerides of the most frequently occurring fatty acids are collated in the following table, in which their chemical formulæ and molecular weights are given, as also the quantities in p.c. of fatty acids and glycerol resulting from saponification of 100 parts of the glycerides:—

1 Glyceride	2 Formula	3 Molecular weight	4 Products obtained on saponification of 100 parts		5 Excess over 100 parts	6 Chief sources
			Fatty acids	Glycerin		
			p.c.	p.c.	p.c.	
Glyceryl tributyrate (Butyrin)	$C_3H_5(O\cdot C_4H_7O)_3$	302	87·44	30·46	17·90	Milk fats
,, tricaproate (Caproin)	$C_3H_5(O\cdot C_6H_{11}O)_3$	386	90·15	23·96	14·11	Milk fats, cocoa-nut oil, palm-nut oil
,, tricaprylate (Caprylin)	$C_3H_5(O\cdot C_8H_{15}O)_3$	470	91·91	19·58	11·49	,, ,, ,,
,, tricaprate (Caprin)	$C_3H_5(O\cdot C_{10}H_{19}O)_3$	554	93·14	16·67	9·81	,, ,, ,,
,, trilaurate (Laurin)	$C_3H_5(O\cdot C_{12}H_{23}O)_3$	638	94·04	14·42	8·46	Laurel oil, cocoa-nut oil, palm-nut oil, dika fat
,, trimyristate (Myristin)	$C_3H_5(O\cdot C_{14}H_{27}O)_3$	722	94·75	12·74	7·49	Myristica fats
,, tripalmitate (Palmitin)	$C_3H_5(O\cdot C_{16}H_{31}O)_3$	806	95·29	11·42	6·71	Palm oil, Chinese vegetable tallow, Japan wax
,, tristearate (Stearin)	$C_3H_5(O\cdot C_{18}H_{35}O)_3$	890	95·73	10·34	6·07	Cacao butter, tallow
,, trioleate (Olein)	$C_3H_5(O\cdot C_{18}H_{33}O)_3$	884	95·70	10·41	6·11	Olive oil, lard oil, tallow oil
,, trilinolate (Linolin)	$C_3H_5(O\cdot C_{18}H_{31}O)_3$	878	95·67	10·48	6·15	Drying and semi-drying oils
,, trilinolenate (Linolenin)	$C_3H_5(O\cdot C_{18}H_{29}O)_3$	872	95·63	10·55	6·18	Drying oils
,, triclupanodonate (Clupanodonin)	$C_3H_5(O\cdot C_{18}H_{27}O)_3$	866	95·61	10·62	6·23	Marine animal oils
,, triricinoleate (Ricinolein)	$C_3H_5(O\cdot C_{18}H_{33}O_2)_3$	932	95·93	9·87	5·80	Castor oil
,, triarachidate (Arachin)	$C_3H_5(O\cdot C_{20}H_{39}O)_3$	974	96·09	9·45	5·54	Earth-nut oil
,, trierucate (Erucin)	$C_3H_5(O\cdot C_{22}H_{41}O)_3$	1052	96·39	8·74	5·13	Rape oils

From the above formulæ it appears that glycerol is regarded as a trivalent, or triatomic alcohol, containing the radicle C_3H_5 in combination with three OH groups. Hence, glycerol bears the same relation to ordinary ethyl alcohol as orthophosphoric acid bears to nitric acid. Just as tribasic phosphoric acid forms three distinct classes of salts, with three different proportions of the same base, so does glycerol form three distinct classes of esters, viz. monoglycerides, diglycerides, and triglycerides (*see* OILS, FIXED, AND FATS). And just as phosphoric acid may combine with two or three different bases to form two different classes of tribasic salts, so does glycerol lead to different classes of triglycerides. Each triglyceride enumerated in the foregoing table must be considered as glycerol in which all three hydrogen atoms of the three OH groups are replaced by one and the same radicle of fatty acid. Such glycerides are termed *simple triglycerides.* If, however, the three hydrogen atoms are replaced by two or three different fatty acid radicles, then *mixed glycerides* are obtained.

In case a triglyceride contains two different fatty acid radicles, then two isomeric triglycerides may be expected; and in case a triglyceride contains three different acid radicles, then three isomerides may be expected. This is explained by the following formulæ :—



It was formerly assumed that the natural fats consist of simple triglycerides; modern researches, however, have made it extremely likely that simple triglycerides occur in nature, as a rule, in small quantities only, and that natural oils and fats are composed chiefly of mixed glycerides. Thus, for instance, in tallow, only a few p.c. of tristearin have been found; hence tallow must be assumed to consist mainly of mixed glycerides.

A considerable number of mixed glycerides have been already isolated from such natural oils and fats as tallow, cacao butter, Borneo tallow, &c. The most frequently occurring mixed glycerides which have been isolated hitherto are *oleodipalmitin*, *stearodipalmitin*, *oleopalmitostearin*, *palmitodistearin*, *oleodistearin*, and *dioleostearin*.

Glycerin has also been found, in the free state, in the blood and in fermented alcoholic liquors. Pasteur has shown that glycerin is a constant product of the alcoholic fermentation of sugar; hence it is a natural constituent of beer, wine, &c. 100 parts of sugar produce 3·5 parts of glycerin. As these latter sources of glycerin are of no commercial importance, and as the synthetic preparation of glycerin has only theoretical interest, we shall here only consider the production of glycerin on a manufacturing scale.

Glycerin is obtained on a large scale in the several saponification processes which are practised in candle and soap works (*see* SAPONIFICATION). According to the process by which the commercial product 'crude glycerin' is obtained, we differentiate in commerce the following five qualities of crude glycerin, viz.: (1) crude saponification glycerin; (2) crude distillation glycerin; (3) Twitchell crude glycerin; (4) fermentation crude glycerin; (5) soap lye glycerin, or soap crude glycerin.

In the stearine candle and soap industries, glycerin is obtained as a dilute aqueous solution, which contains various impurities, the nature and quantity of which depend on the manufacturing processes themselves. The purest raw material results from saponification by means of lime in open vessels; hardly inferior to this is the glycerin obtained by 'autoclaving.' Less pure is the raw material recovered from the 'acid saponification process,' 'Twitchell's process,' and the 'ferment process.' The crude glycerin obtained from soap lyes, notwithstanding its high proportion of inorganic salts, may, on the one hand, surpass in purity (*i.e.* as regards the amount of organic impurities) the crude material from the last-named processes; but, on the other hand, it may be very impure if fats and oils of low quality have been saponified by means of black-ash lyes, as was done in Lancashire and in Marseilles up to recently. Modern processes of refining have, however, overcome a number of difficulties caused by the several impurities, so that *e.g.* chemically pure glycerol from good soap lyes cannot be distinguished from chemically pure glycerol obtained by lime saponification. Crude glycerins further vary as regards quality in accordance with the care exercised in the manufacture. Crude glycerins obtained from the acid saponification, the Twitchell, and the ferment processes, retain very tenaciously some organic impurities which hitherto seem to have defied all attempts to remove them, as the writer has ascertained in

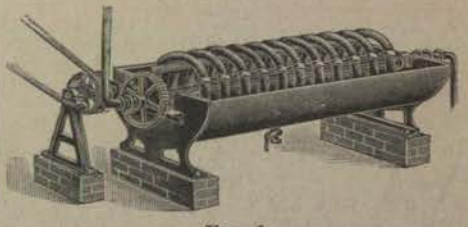


FIG. 1.

the case of a number of 'chemically pure' glycerols originating from these processes.

1. **Crude saponification glycerin.** This glycerin represents the best quality of crude glycerin. It is obtained from the 'sweet water' of the autoclave process (*see* SAPONIFICATION) and as a by-product in the process of soap making by double decomposition.

The proportion of glycerol in the 'sweet waters' varies from 6 to 16 p.c. The metallic oxides contained in the 'sweet waters' are neutralised, and the filtered solution is concentrated by means of steam, either in a Wetzel pan

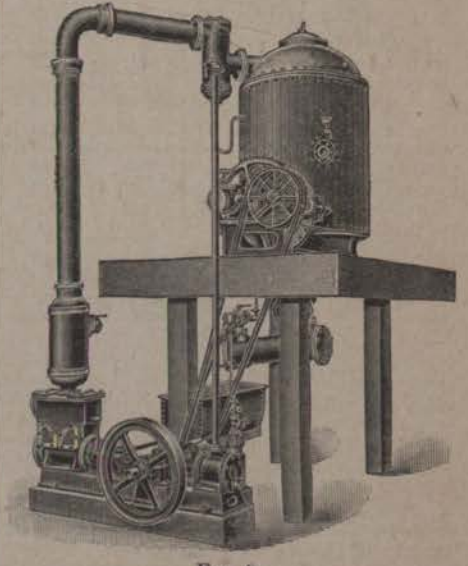


FIG. 2.

(Fig. 1) or, as is done in modern works, in a vacuum evaporator of a type identical with or

similar to those shown in Figs. 2, 3. According to the quantity of salts which separate when the bulk of water has been driven off, a vacuum evaporator either of the type A or type B (Fig. 4) is used. The evaporation is carried on until the crude glycerin contains about 85–90 p.c. of glycerol. Its sp.gr. is then from 1·240 to 1·242, corresponding to the commercial brand of '28°Bé saponification crude' or 'candle crude glycerin.' The colour of this glycerin varies from yellow to dark-brown; its taste is sweet. With basic lead acetate, it gives but a slight precipitate. By refining this crude glycerin with charcoal, a 'refined' glycerin (used for a number of commercial purposes) is obtained. This crude glycerin contains up to 0·3 p.c. of ash, chiefly calcium (or magnesium or zinc) sulphate, and only small quantities of organic impurities.

This crude glycerin is valued on the percentage of pure glycerol, of ash, and of organic impurities.

The 'sweet water' obtained in the process of soap making by double decomposition is treated in the same manner as described above, and yields a good 'saponification crude,' which is equal in quality to a 'candle crude glycerin,' provided that the original fatty matter was of good quality. Since this process is used in small works only, where chiefly low-quality greases are worked up, the crude glycerin thus obtained is apt to contain a considerable amount of organic impurities, so that it is liable to ferment when stored. Within the author's experience, such crude glycerins did ferment, thus showing that the organic substances in low-class grease are not destroyed by treatment with lime. In the course of the fermentation, trimethyleneglycol is formed. This crude glycerin is also high in proportion of ash (the author found even as much as 1·77 to 5 p.c. of ash), whereas the respective proportions of glycerol were 84·3 and 77·1 p.c.

2. **Crude distillation glycerin.** This kind of crude glycerin is obtained from the acid water resulting in the so-called acid saponification processes (*see* SAPONIFICATION). It is termed in commerce 'crude distillation glycerin' for the reason that the fatty acids obtained by this process must be distilled to yield candle material. The dilute glycerin waters ('sweet waters') are worked up in the same manner as described under 'crude saponification glycerin,' but owing to the large amount of sulphuric acid used in the process, a considerable quantity of salts remain in solution after the mineral acid has been neutralised with lime. As the concentration of the solution proceeds, especially when the thickened liquor approaches the sp.gr. of 1·240, sulphate of lime, which is no longer held in solution, drops out, and is deposited on the heating surface of the evaporating apparatus in the form of a hard crust, which rapidly diminishes the evaporative power of the steam, unless the calcium sulphate is removed.

Hence, such tube evaporators as are represented by vessel B (Fig. 4) are useless for concentrating the dilute solution, and a type of evaporator must be employed which permits the heating surface to be continuously scraped so as to keep it clean. An evaporator of this kind, designed by the author, is shown in Fig. 2, the inner construction of which is exemplified by Fig. 3.

The finished crude distillation glycerin contains considerable proportions of calcium sulphate, inasmuch as the solvent power of glycerol for calcium sulphate (*see* below) is still further increased by the organic impurities which the crude glycerin retains. The ash of this kind of crude glycerin rises to as much as 2 and even 3·5 p.c. The amount of organic impurities is greater than in crude saponification glycerin,

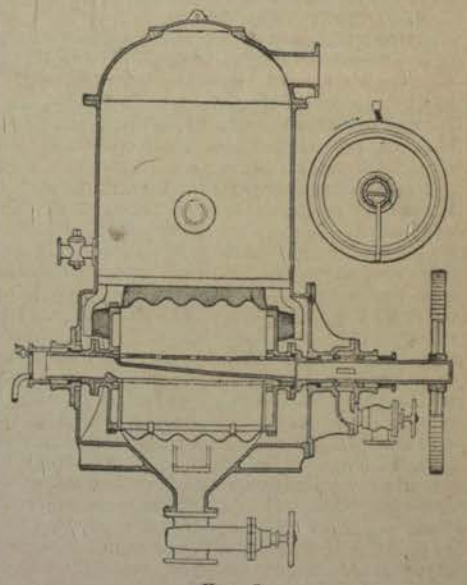


FIG. 3.

and it may rise to even 2 p.c., the amount depending on the lack of care exercised in the manufacturing process. The colour of this crude glycerin is usually pale-yellow; its taste is sharp and astringent, and when rubbed between the hands it emits an unpleasant smell. On adding basic lead acetate, a voluminous precipitate is obtained; hydrochloric acid produces a turbidity, due to the presence of fatty acids.

This crude glycerin has the sp.gr. 1·240–1·242. As a rule, it contains from 84 to 86 p.c. of glycerol. The trade term for this kind of glycerin is 'crude distillation glycerin, 28°Be.'

3. **Crude glycerin from the Twitchell process.** This kind of crude glycerin is obtained from the acid water resulting in Twitchell's saponification process (*see* SAPONIFICATION). The sweet waters are treated with lime or barium hydrate or barium carbonate, so as to precipitate the dissolved sulphuric acid as completely as possible. The purified liquors are concentrated up to a sp.gr. of about 1·24 or more, in the same manner as described under the two preceding headings. The quality of this crude glycerin varies considerably with the quality of the fatty material from which it has been obtained. If the raw material is of good quality, the glycerin is fairly good; but even in that case, owing to the high amount of ash it contains, and owing to its unpleasant taste, it is valued at a somewhat lower

price than is crude candle glycerin. By way of example, the following analysis made by the author, may be given: sp.gr. 1·239; glycerol, 84·8 p.c.; ash, 0·52 p.c. Since the Twitchell saponification process is best adapted to low-class material (such as greases), the glycerin obtained from such material contains so considerable an amount of organic impurities that it cannot be refined by itself, not even for the production of dynamite glycerin. Each special make of such glycerin must therefore be valued on the basis of the impurities it contains.

4. Fermentation crude glycerin (*see* SAPONIFICATION). The sweet water from the process of hydrolysis by means of ferments is rich in albuminoids and other organic impurities. In addition to the usual treatment described above, it must be filtered over char, which retains the bulk of the albuminoids and other organic impurities. Nevertheless, a certain amount is still retained; consequently, the finished crude is not only dark in colour, but has also a very unpleasant smell and taste, even if the glycerin be made from good raw material, such as refined cotton-seed oil or refined linseed oil. In the infancy of the process, the crude glycerin obtained thereby was practically unusable. In consequence of improvements made more recently, the amount of impurities has been considerably reduced, so that a sample examined in the author's laboratory gave the following somewhat favourable results: sp.gr. 1·2369; ash, 0·49 p.c.; organic impurities (albuminoids, &c.), 1·54 p.c. The last two kinds of crude glycerin are difficult to refine (by the usual process of distillation) and must be mixed in the glycerin still with better kinds of crude glycerin.

5. Soap lye glycerin, Soap crude glycerin, Soap crude. Since Chevreul established the constitution of fats and oils, it has been known that the spent soap lyes, resulting in the manufacture of soap, contain, if not the whole, a very large proportion of the glycerol, combined originally with fatty acids in the oils and fats which had been converted into soap in the soap pan. During the first half of last century, no attempt had been made to recover the glycerin from those lyes, not only on account of the difficulty attending this operation, but also for the reason that the small demand for glycerin then ruling in the market could be readily satisfied by the candle makers' crude glycerin. When, at the end of the 'seventies of the last century, a great demand for nitroglycerin ('dynamite') sprang up, attention was drawn forcibly to this source of glycerin, and serious endeavours were made to recover the hitherto wasted product. Although as early as 1858, H. Reynolds had patented the main features of a process of recovery, features which essentially reappeared in all subsequent processes, yet serious failure at first attended all attempts at the recovery of glycerin, on account of the considerable amount of impurities in the spent lyes, and most prominently on account of the large amount of dissolved salts. Modern processes, especially improvements in apparatus on the one hand, and the rapidly growing employment in the soap industry of caustic soda of the highest purity, tended to evolve a process which is now worked with more or less success in all the large soap works, not only of Europe and America, but also of Australia, Africa, India, and New Zealand. The earliest successful attempts to recover glycerin from soap lyes were made in English soap works, where the largest quantities of oils and fats were worked up in the largest soaperies of the world; the working up of the soap lyes for crude glycerin may be said to have established its success in Great Britain towards the middle of the 'eighties of the last century. Since that time, crude glycerin recovered from soap lyes, 'soap crude glycerin,' has established its great importance in the world's commerce.

The lyes obtained in the soap-making process by boiling oils and fats in an open pan with caustic soda contain practically all the glycerol which the natural oils and fats are capable of yielding. According to the manner in which the 'changes' are worked up (*see* SOAP), the spent lyes contain from 5 to 8 p.c. of pure glycerol. In addition to glycerol, the spent lyes hold in solution the common salt used in 'cutting' the soap, and also small amounts of free caustic soda, sodium carbonate, soap, and organic impurities. The less free caustic soda, sodium carbonate, and organic impurities the lyes contain, the more readily can the process of recovery and purification be carried out. In case impure caustic soda lyes have been used (*see* above), the spent soap lyes contain, in addition to the substances enumerated above, sulphocyanides, sulphides, hyposulphites, cyanides, and ferrocyanides. These impurities result from the crude (black-ash) lyes, which were used up to a few years ago to a large extent in the Marseilles district. The difficulties caused thereby in the recovery of crude glycerin has led, favoured by the establishment of Solvay's soda works in that neighbourhood, to the almost complete abandonment of black-ash lyes, so that even in Marseilles the vast majority of soaps are prepared with pure caustic lyes. The exact treatment of the lyes in a soap works depends on the state of purity of these lyes, and has, as its object, the removal or destruction of the albuminous, resinous, and soapy matters present in the lyes. This is done by various additions, such as lime or hydrochloric acid, or salts of aluminium and iron, which precipitate foreign substances, so that they can be filtered off, whereupon the purified lyes are neutralised and become ready for concentration. The purified lyes are boiled down in fire-heated vessels, which are of a conical shape, so that the salt, as it separates, slides down into a vessel fixed to the bottom of the pan, whilst rotating gear keeps the heating surface free from incrustation. Such vessels, although in large works considered antiquated, are still being used and even at present introduced in smaller works, where the amount of water available is limited or where water is very dear. In the case of large works, the lyes are usually evaporated *in vacuo*. The first concentration of the lyes to the 'salting-point' (at which salt commences to separate) is considered to have been completed when the lyes have reached a sp.gr. of 44°Tw. at 15·5°C. The percentage of glycerol in these lyes then usually amounts to 10–16 p.c. If evaporation were carried on beyond this 'salting-point' in a tube evaporator, the separated salts would deposit on the tubes, and thus soon prevent

the evaporation from proceeding to the desired stage. The author has frequently seen tube evaporators, which, after a couple of days' working, became so heavily encrusted with salts that the evaporator had to be stopped and 'laid off' for cleaning. A large number of patents have been taken out, even up to the most recent date, with a view to preventing the settling down of the salts on the evaporator tubes. Lewkowitsch overcomes this difficulty by providing the evaporator with suitable stirring and scraping arrangements, which remove the salts as they separate, the salts falling down into a vessel (of any desired shape) which can be shut off from the vacuum evaporator, and emptied at will under ordinary pressure. After emptying the salt, the vessel is exhausted and again connected with the evaporator. An evaporator of this type is shown in Fig. 2. The construction of the rotating heating surface is typified by Fig. 3. In these evaporators, the soap lyes can be evaporated from their dilute stage beyond the 'salting-point,' the salt which falls out being removed by using, at given intervals, the vessel fixed to the outlet of the evaporating pan. This vessel, as has been pointed out already, can be emptied whilst the contents are kept continuously boiling. In large installations, the lyes are concentrated in double, or triple, or quadruple effect vacuum apparatus. A double effect, designed by Lewkowitsch on the same principle as Fig. 2, is illustrated by Fig. 4.

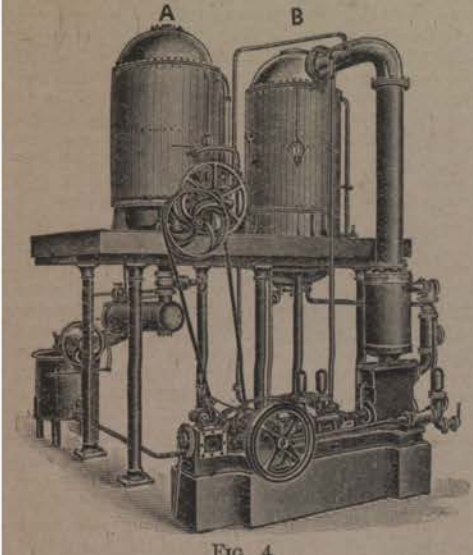


FIG. 4.

This figure shows a combination of a tube evaporator, B, with an evaporator as illustrated by Fig. 2. The first preliminary concentration up to the 'salting-point' is carried out in vessel B, whilst the further concentration takes place in vessel A. The salt which separates out during the process of concentration is collected in the vessel shown underneath A, and is removed at fixed times, and washed in the washing machine shown in the illustration. The salt is washed first with purified lyes of low percentage of glycerol, and finally with water to remove the glycerin from the salt. The salt itself is recovered in such purity that it can be used immediately in the soapery in place of fresh salt (*see* SOAP).

The glycerin solutions are boiled *in vacuó* until the crude glycerin has reached a sp.gr. of 1·3. The progress of concentration is controlled by the sp.gr. test, or, equally well, by taking out samples and ascertaining the boiling-point in a porcelain dish, by means of a thermometer, whilst the contents of the dish are kept stirred, so that the salt may not cause bumping of the contents or cracking of the dish. The glycerin has reached the sp.gr. of 1·3 and the percentage required by commerce, if the boiling-point is 150°. The crude glycerin then contains 80 p.c. of pure glycerol, and about 10 p.c. of salts, the remainder consisting of water and a small amount of organic impurities. If the concentration is carried a little further, crude glycerin, containing as much as 86 p.c. of glycerol, can be obtained readily.

The proportion of organic impurities in soap-lye glycerin varies considerably, depending on the process of purification and the care of the operator. Some commercial soap crude glycerins contain less than 1 p.c. of organic impurities (thus representing a better quality glycerin than 'crude distillation glycerin,' crude glycerin from the 'Twitchell process,' and crude glycerin from the 'fermentation process'). Other specimens of crude glycerin, again, contain large quantities of impurities, consisting of fatty acids, rosin acids, and of albuminoid substances, gelatin, and hydrocarbons (from bone fat), and also trimethyleneglycol in the lyes resulting from bone fat which has been allowed to ferment. In the distillates from such impure glycerins, the author even found organic bases, amongst which he identified picoline and lutidine.

The colour of 'salt crude glycerin' is pale-yellow to brown, or almost black, according to its purity. The taste of good 'soap crude' is sweet, qualified, of course, by that of the common salt contained therein. Impure samples have a most unpleasant garlic-like taste, even if sulphides be absent. This is specially characteristic of the lyes obtained in the Marseilles district (due to the use of sulphur olive oil).

Soap lye glycerin can be rapidly distinguished from the crude glycerins described above by the large proportion of common salt which it contains (heavy precipitate with silver nitrate solution) and by its high sp.gr.

A soap lye glycerin containing considerable quantities of sulphides, thiosulphates, or sulphites, is almost valueless to the refiner of crude glycerin.

Considerable quantities of crude glycerin, especially crude saponification glycerin, are used in the arts for various purposes. By far the largest quantities of crude glycerin are, however, purified by distillation, and thereby converted into 'distilled glycerin.' In commerce, two kinds of distilled glycerin are differentiated, distilled glycerin for making nitroglycerin (dynamite), 'dynamite glycerin,' and chemically pure glycerin, sometimes termed 'twice-' or 'treble-distilled glycerin.'

Distilled glycerins are obtained, as the name

implies, from crude glycerin by distillation. The distillation is carried out, either under ordinary pressure or in a vacuum. In either case the distillation is supported and accelerated by the aid of steam. At present vacuum distillation, coupled with superheated steam, is the combination mostly in vogue. Some manufacturers work off a certain amount (depending on the size of the still) of crude glycerin in one batch. Other manufacturers resort to continuous distillation, the still being fed as the glycerin distils off.

The successful distillation of crude glycerin does not so much depend on the kind of still and condensers used as on the skill and care of the operator. A considerable number of special apparatus have been patented, and are still being patented, but owing to the fact pointed out, viz. that success depends more on attention to details than on the particular apparatus employed, the details of the *modus operandi* in conducting the distillation are considered valuable secrets.

Space does not permit a complete reference to the patent literature or to the illustrations accompanying it. It may therefore be generally stated that some inventors introduce details which neither contribute to cheapening the process nor permit the realisation of the refinements claimed. Some of the apparatus embody a faulty principle, inasmuch as not only no complete purification is effected, but even partly purified distillates are contaminated with the impurities driven off from a partially purified batch. Here it may suffice to illustrate in Fig. 5 a glycerin distillation plant which the

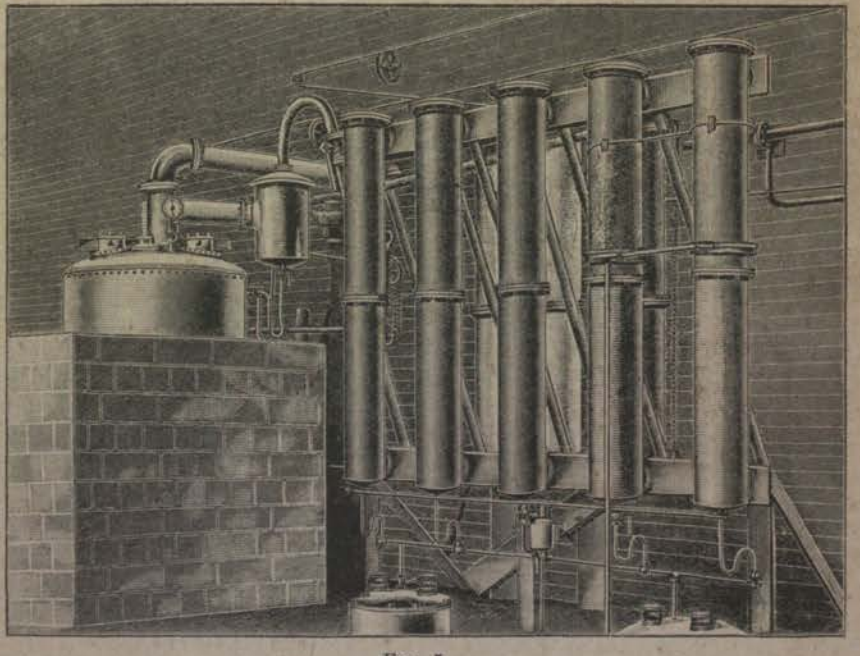


FIG. 5.

author has designed for the distillation of crude glycerins, both of 'saponification crude' and 'soap crude.' The still shown is provided with an arrangement for withdrawing the salts as they separate out. The contents of the still are heated by means of open superheated steam, which carries off the vapours of glycerin into a battery of condensing columns. Between the latter and the still itself is inserted a catch box in which the heaviest portions are condensed together with small amounts of sodium chloride, which is carried over mechanically with the steam. From the end of the battery of columns a connection leads to a vacuum pump, the distillation being carried out *in vacuo*. The glycerin vapours, with varying amounts of water, condense in the several columns. In the first columns little water condenses; thus the strongest glycerin, of sp.gr. 1·25, is obtained therein. The following columns yield weaker glycerin liquors which, in the end column, are so dilute that the then escaping vapours are practically free from volatilised glycerin. The distillates are drawn off *in vacuo*, sampled and graded according to their sp.gr. In the figure, the vessels into which the glycerin is drawn off are partly shown.

It depends solely on the mode of working—especially in the case of soap lye glycerin—as to whether one distillation will suffice to obtain a satisfactory product for nitrating purposes, or whether the once distilled glycerin must be redistilled. In case the distillation has not been conducted carefully, the once-distilled glycerin is so strongly contaminated with sodium chloride and organic impurities (volatile fatty acids and even polyglycerols), that a second distillation becomes imperative.

The distilled glycerin liquors collected from the columns are treated with char, if required,

in order to remove some organic impurities, and, at the same time, to clarify the glycerin and improve its colour. The collected and filtered glycerin liquors are finally concentrated in a vacuum evaporator, up to the desired sp.gr. For the purposes of dynamite glycerin, the sp.gr. must be at least 1·261 at 15°. Other commercial qualities of distilled glycerin need only be concentrated to a sp.gr. of 1·250 or 1·240, as the case may be. The dynamite glycerin quality is used exclusively for purposes of making nitroglycerin. Other qualities of distilled glycerin, especially those of sp.gr. 1·250 and 1·240, are used for various purposes in the arts, such as for filling gas meters and hydraulic jacks, in the manufacture of ink, waterproof paper, toilet soaps, 'sizes' for textiles, and for the production of plastic masses, such as printing rollers, hectograph mass, &c. The bulk of the distilled glycerin is, however, employed in the manufacture of high explosives, such as dynamite, blasting gelatine, cordite, &c.

The yield obtainable from crude glycerin depends, just like the distillation itself, on the care of the operator. The losses incurred by faulty methods are large, and range, within the knowledge of the author, from as much as 15 to even 40 p.c. A large proportion of the loss is due to destruction of glycerol with the formation of volatile acids and acroleïn on the one hand, and to the formation of polyglycerols on the other hand. The polyglycerols which are formed in the course of distillation should remain in the still itself, and are found with the still residue (*see* below, *Glycerine foots*).

The commercial 'distilled glycerins' vary in colour from yellow to white; they also vary in their content of glycerol according to their sp.grs., which range, as a rule, between 1·220 and 1·260. Glycerin, purified by distillation, should contain a very small amount of ash only; thereby distilled glycerins are easily distinguished from crude glycerins.

The residues ('*glycerin foots*') remaining in the still, in the case of those crude glycerins which contain small proportions of ash (*see* above, *Crude glycerins*, 1, 2, 3, 4), consist chiefly of polyglycerols and of notable amounts of salts, as the mineral matters originally contained in the crude material naturally accumulate in the residues. These residues are used in the manufacture of shoe blacking. Claessen proposed to employ them also in the production of plastic masses, such as printing rollers, hectograph masses, sizes for textiles, and for waterproofing paper.

The still residues from soap lye crude contain much larger amounts of salts than those described above. The residues obtained in the *course of distillation* retain such considerable amounts of glycerol in addition to polyglycerol, salt, sodium carbonate, sodium acetate, and sodium salts of other organic non-volatile acids, that the accumulated residues are worked up for the recovery of glycerin. They are boiled up with water, and dilute hydrochloric or sulphuric acid is added to decompose the sodium carbonate and the organic salts. The organic non-volatile acids collect on the surface of the liquid as a resinous mass, which is removed in any suitable manner. The liquor is then filtered and concentrated separately, or is admixed to the ordinary soap lyes. As during the concentration of these liquors, acetic acid is volatilised, it is advisable to concentrate the lyes and distil the recovered crude glycerin separately.

The distilled glycerins described above contain, as a rule, although small, yet sufficiently large amounts of impurities to forbid the employment of those distilled glycerins for pharmaceutical and dietetic purposes. The 'distilled glycerins' must therefore, as a rule, be subjected to a second distillation. If this distillation be carried out with sufficient care, the distillates give, after concentration, and treatment with char, the chemically pure glycerin of commerce.

At a time when the art of preparing chemically pure glycerin was not so far advanced as it is at present, some chemically pure glycerin was manufactured by allowing glycerin to crystallise, and centrifugalising the crystals, whereby the impurities were removed with that portion of glycerin which melted in the centrifugal machine. This process has, however, been abandoned, not only on account of its costliness, but also on account of the inferiority of the product as compared with the best brands of chemically pure glycerin obtained by careful distillation, as it was found that the crystals were apt to occlude impurities.

The statements found in chemical literature that glycerin only crystallises at −40°, must be corrected, in so far as glycerin, exposed for a long time to a low temperature (−5° or −10°), will gradually crystallise. Thus the author frequently found in very cold winters that glycerin, even glycerin of 'dynamite quality' which had been left undisturbed for some prolonged time, had crystallised.

Chemically pure glycerin is obtainable in commerce in the following 'strengths' (concentrations): chemically pure glycerin of 1·24 sp.gr., chemically pure glycerin of 1·25 sp.gr., and chemically pure glycerin of 1·26 sp.gr.

The chemically pure glycerin of the highest sp.gr. (*see* below) approaches, as nearly as is possible for a product made on a large scale, the chemical substance glycerol.

Glycerol (pure glycerin) is an odourless, colourless, viscid liquid, having an intensely sweet taste. The preparation demanded by the Pharmacopœias of different countries is the purest commercial article which consists practically of glycerol, containing a very small amount of water. Glycerol is optically inactive, and is neutral to indicators. On exposure to an intense cold for a prolonged time, it crystallises in rhombic crystals, melting at 20°. With the help of a few crystals, large quantities of glycerol can easily be solidified at the temperature of the freezing-point of water.

Glycerin is oily to the touch, and produces on the skin, especially on the mucous membrane, the sensation of heat, due to its absorbing moisture from the tissues. The water-absorbing power of glycerin is so great that, on exposure to the atmosphere, as much as 50 p.c. of its own weight of water is taken up.

The sp.gr. of pure glycerin has been determined by several observers, whose statements do not agree, owing, no doubt, to the difficulty of freeing it from the last traces of water. The most reliable values are the following:—

sp.gr. $15°/15° = 1·26468$;
sp.gr. $17·5°\ 17·5° = 1·2620$.

Provided a specimen of chemically pure glycerin satisfies the qualitative tests described below, the proportion of glycerol in it can be found by merely determining the sp.gr. of the sample. The percentage can also be obtained, approximately, from the refractive index of the glycerin. The following table by Skalweit (Repertor. d. Analyt. Chemie, 5, 18) gives the sp.grs. and refractive indices, for the sodium ray, at 15°, of mixtures of glycerol and water in various proportions :—

Glycerol, p.c.	Sp.gr. at 15° compared with water at 15°	Refractive index at 15°	Glycerol, p.c.	Sp.gr. at 15° compared with water at 15°	Refractive index at 15°
0	1·0000	1·3330	51	1·1318	1·4010
1	1·0024	1·3342	52	1·1346	1·4024
2	1·0048	1·3354	53	1·1374	1·4039
3	1·0072	1·3366	54	1·1402	1·4054
4	1·0096	1·3378	55	1·1430	1·4069
5	1·0120	1·3390	56	1·1458	1·4084
6	1·0144	1·3402	57	1·1486	1·4099
7	1·0168	1·3414	58	1·1514	1·4104
8	1·0192	1·3426	59	1·1542	1·4129
9	1·0216	1·3439	60	1·1570	1·4144
10	1·0240	1·3452	61	1·1599	1·4160
11	1·0265	1·3464	62	1·1628	1·4175
12	1·0290	1·3477	63	1·1657	1·4190
13	1·0315	1·3490	64	1·1686	1·4205
14	1·0340	1·3503	65	1·1715	1·4220
15	1·0365	1·3516	66	1·1743	1·4235
16	1·0390	1·3529	67	1·1771	1·4250
17	1·0415	1·3542	68	1·1799	1·4265
18	1·0440	1·3555	69	1·1827	1·4280
19	1·0465	1·3568	70	1·1855	1·4295
20	1·0490	1·3581	71	1·1882	1·4309
21	1·0516	1·3594	72	1·1909	1·4324
22	1·0542	1·3607	73	1·1936	1·4339
23	1·0568	1·3620	74	1·1963	1·4354
24	1·0594	1·3633	75	1·1990	1·4369
25	1·0620	1·3647	76	1·2017	1·4384
26	1·0646	1·3660	77	1·2044	1·4399
27	1·0672	1·3674	78	1·2071	1·4414
28	1·0698	1·3687	79	1·2098	1·4429
29	1·0724	1·3701	80	1·2125	1·4444
30	1·0750	1·3715	81	1·2152	1·4460
31	1·0777	1·3729	82	1·2179	1·4475
32	1·0804	1·3743	83	1·2206	1·4490
33	1·0831	1·3757	84	1·2233	1·4505
34	1·0858	1·3771	85	1·2260	1·4520
35	1·0885	1·3785	86	1·2287	1·4535
36	1·0912	1·3799	87	1·2314	1·4550
37	1·0939	1·3813	88	1·2341	1·4565
38	1·0966	1·3827	89	1·2368	1·4580
39	1·0993	1·3840	90	1·2395	1·4595
40	1·1020	1·3854	91	1·2421	1·4610
41	1·1047	1·3868	92	1·2447	1·4625
42	1·1074	1·3882	93	1·2473	1·4640
43	1·1101	1·3896	94	1·2499	1·4655
44	1·1128	1·3910	95	1·2525	1·4670
45	1·1155	1·3924	96	1·2550	1·4684
46	1·1182	1·3938	97	1·2575	1·4698
47	1·1209	1·3952	98	1·2600	1·4712
48	1·1236	1·3966	99	1·2625	1·4728
49	1·1263	1·3981	100	1·2650	1·4742
50	1·1290	1·3996			

Other tables for the sp.gr. and the refractive indices of glycerol solution are given in Lewkowitsch's Chem. Technology of Oils, &c., 326, 327. Lenz states that the observations of the several observers agree amongst each other to a few units of the fourth decimal, whilst the differences in the refractive indices, corresponding to 1 p.c. of glycerol, amount to 13·5 units of the fourth decimal. By reference to the above table, the percentage of glycerol in a sample can therefore only be determined accurately to 0·5 p.c.

Where the volume of glycerin is not enough to permit the accurate determination of its sp.gr., the refractive index can be ascertained with the aid of Abbe's refractometer. Recently Zeiss's immersion refractometer has also been applied to the determination of dilute glycerin solutions; but it should be noted that the immersion refractometer (which is used extensively for the determination of alcohol in beer and other fermented liquors) does not permit more concentrated solutions to be tested than those containing 26 p.c. It is not permissible to dilute concentrated glycerin with a known amount of water to a lower percentage, and then determine the refractive index, inasmuch as contraction takes place on mixing glycerin with water.

Glycerin boils under 760 mm. pressure at 290°, when it undergoes only slight decomposition. Under considerably reduced pressure, glycerin distils unchanged.

The following table contains the most reliable observations made under reduced pressures (*cf. also* Richardson, Chem. Soc. Trans. 1886, 49, 746) :—

Pressure mm.	Boiling-point (°.
385·33	260·4
347·10	257·3
231·87	250·3
201·23	241·8
100·81	220·3
50·00	210·0
45·61	201·3
30·00	191·8
20·46	183·3
12·50	179·5
10·00	167·2
6·53	161·3
5·00	155·5
0·24	118·5
0·056	115–116

Glycerol is miscible with water in all proportions. On mixing glycerol with water, a contraction of volume and an increase of temperature takes place. The greatest increase of temperature, viz. 5°, is observed when 58 parts of glycerol (by weight) are mixed with 42 parts of water: the greatest contraction equals 1·1 p.c. (Gerlach). Glycerin can be completely freed from water by allowing it to stand *in vacuô* over sulphuric acid for some prolonged time.

At the ordinary temperature, glycerol does not volatilise; at the boiling-point of water, however, appreciable quantities escape with the water vapours. If glycerol be heated in an open dish on a water-bath, a slight loss is incurred, such loss depending on the shape of the vessel (whether deep or shallow), the area of the surface exposed, and the frequency with which the air over its surface is renewed.

The vapour pressure of a dilute solution of glycerol rises with the rise of temperature of the boiling solution, so that considerable amounts of glycerol volatilise with the water vapour. Theoretically, a mixture of saturated water and glycerol vapour, under the ordinary atmospheric pressure, cannot contain more than 0·2 to 0·3 p.c. of glycerol, provided that the two vapours are not miscible. Since, however, glycerol and water are miscible in every proportion, the composition of the escaping vapours cannot be calculated according to Dalton's law, but must be derived from actual observations. Gerlach determined, with the aid of a vaporimeter, in which the pressure of the vapour was measured by a column of mercury, the vapour pressures given in the following table:—

VAPOUR TENSIONS OF GLYCEROL AND OF AQUEOUS SOLUTIONS OF GLYCEROL (GERLACH).

Glycerol, p.c.	Water p.c.	B.p. at 760 mm. pressure °C.	Vap. pressure at 100°C.
100	0	290	64
99	1	239	87
98	2	208	107
97	3	188	126
96	4	175	144
95	5	164	162
94	6	156	180
93	7	150	198
92	8	145	215
91	9	141	231
90	10	138	247
89	11	135	263
88	12	132·5	279
87	13	130·5	295
86	14	129	311
85	15	127·5	326
84	16	126	340
83	17	124·5	355
82	18	123	370
81	19	122	384
80	20	121	396
79	21	120	408
78	22	119	419
77	23	118·2	430
76	24	117·4	440
75	25	116·7	450
74	26	116	460
73	27	115·4	470
72	28	114·8	480
71	29	114·2	489
70	30	113·6	496
65	35	111·3	553
60	40	109	565
55	45	107·5	593
50	50	106	618
45	55	105	639
40	60	104	657
35	65	103·4	675
30	70	102·8	690
25	75	102·3	704
20	80	101·8	717
10	90	100·9	740
0	100	100	760

Up to a concentration of about 50 p.c., no glycerol escapes with the water vapours, even if the dilute solutions be kept boiling for a prolonged time. At a concentration of about 70 p.c., traces of glycerol escape from the boiling solution (Hehner). The boiling-point of such a solution is 113·6° (*see* table). Above this concentration, noticeable amounts of glycerol escape, so that the quantitative determination of glycerol in an aqueous solution by evaporating it down on the water-bath leads to faulty results. Even if the concentration of glycerol solutions be carried out *in vacuô*, considerable proportions of glycerol escape with the water vapour when the concentration of the solution exceeds 80 p.c. (Lewkowitsch).

Glycerol is miscible with alcohol in all proportions. It dissolves easily in a mixture of alcohol and ether, but is sparingly soluble in ether alone, one part of glycerol, sp.gr. 1·23, requiring about 500 parts of ether. It is therefore impossible to extract glycerol from its aqueous solution by means of ether. Glycerol is soluble in acetone. Nine parts of glycerol dissolve in 100 parts of ethyl acetate. It is, however, insoluble in chloroform, light petroleum, carbon disulphide, or benzene; it is also insoluble in oils and fats (Lewkowitsch).

On heating glycerol slowly in a platinum dish to 150°–160°, it evaporates gradually without leaving a residue; at 150° it will burn with a bluish non-luminous flame without emitting any odour. If, however, glycerol is heated rapidly in a platinum dish, it burns with formation of acrolein, and yields a residue consisting of polyglycerols.

The penetrating smell of acrolein (which is also noticeable when glycerides are burnt, *e.g.* when an oil lamp or a tallow candle has been blown out) serves as the most characteristic reaction for the detection of the smallest quantities of glycerol. For this purpose, it is best to mix the substance under examination with dehydrating substances, such as potassium hydrogen sulphate, and heat rapidly when acrolein is readily formed. The most delicate reagent for detecting acrolein in an aqueous solution is an ammoniacal solution of silver nitrate (reduction to metallic silver with production of a mirror). With Schiff's reagent, a solution of rosaniline which has been previously decolorised by sulphur dioxide, the pink colour is restored. The latter reaction, however, is less delicate than the silver test.

Glycerol has powerful solvent properties; it combines in this respect the properties of water and of ordinary alcohol; many substances dissolve even more easily in it than in either of these two latter liquids. The following table of solubilities will serve to illustrate this:—

100 parts of glycerol dissolve at 15° 98 parts of crystal soda; 60 parts of borax; 50·5 parts of potassium arsenate; 50 parts of sodium arsenate; 50 parts of zinc chloride; 48·8 parts of tannic acid; 40 parts of alum; 40 parts of zinc iodide; 40 parts of potassium iodide; 35·2 parts of zinc sulphate; 32 parts of potassium cyanide; 30 parts of copper sulphate; 25 parts of ferrous sulphate; 25 parts of potassium bromide; 20 parts of lead acetate; 20 parts of ammonium carbonate; 20 parts of arsenious acid; 20 parts of arsenic acid; 20 parts of ammonium chloride; 15 parts of oxalic acid; 11 parts of boric acid; 10 parts of barium chloride; 10 parts of copper

acetate; 10 parts of benzoic acid; 8 parts of sodium bicarbonate; 7·5 parts of mercuric chloride; 5 parts of calcium sulphide; 3·7 parts of potassium chloride; 3·5 parts of potassium chlorate; 1·9 parts of iodine; about 1 part of calcium sulphate; 0·1 part of sulphur; 0·25 part of phosphorus.

An aqueous glycerol solution, of the sp.gr. 1·114, dissolves 0·957 p.c. of calcium sulphate. Metallic soaps (which are insoluble in water) are to some extent dissolved by glycerol; thus: 100 parts of glycerol, sp.gr. 1·114, dissolve 0·71 part of iron oleate, 0·94 part of magnesium oleate, and 1·18 parts of calcium oleate.

Glycerol is completely oxidised to carbon dioxide and water by potassium dichromate in an acid solution. In a dilute aqueous solution, and in the presence of caustic alkali, potassium permanganate oxidises glycerol so definitely to oxalic acid and carbonic acid (under the conditions stated below) that this reaction may be used for its quantitative determination (provided no other organic substance yielding oxalic acid be present).

Dry potassium permanganate reacts violently with concentrated glycerol. If finely powdered potassium permanganate be heaped up to form a small truncated cone and concentrated glycerol be poured into a hole made on the top, fumes escape; after a very short time the glycerol commences to froth and ignites spontaneously with violent evolution of gases.

By gentle oxidation with nitric acid, glycerol yields glyceric and oxalic acids, together with formic, glycollic, glyoxylic, and racemic acids. The glyceric acid so obtained is a racemic compound which can be resolved into optically active enantiomorphous glyceric acids (Lewkowitsch, Ber. 1883, 2720).

A strong aqueous solution of glycerol reduces Fehling's solution only slightly. On boiling the solution for 10 minutes, and allowing it to stand for 24 to 48 hours, a red or a yellow precipitate is obtained. If, however, the glycerol be diluted previously with 10 times its bulk of water, no reduction occurs.

A mixture of glycerol and silver nitrate solution heated at the temperature of boiling water with a few drops of ammonia, gives a precipitate of metallic silver. If ammonia solution be added to glycerol in the cold, and heat be then applied, as a rule no reduction takes place on adding silver nitrate, because the ammonia escapes before the glycerol has been heated sufficiently; the addition of caustic soda or potash, however, causes metallic silver to separate slowly. According to Bullnheimer, 1 part of metallic silver corresponds to 11·3 parts of glycerol.

Glycerol dissolves caustic alkalis, alkaline earths, and lead oxide, to form chemical compounds with them. The compounds so formed are termed metallic glyceroxides. Lime, strontia, and baryta are precipitated nearly completely from such solutions by carbon dioxide, a small quantity only of the earths escaping precipitation. In the presence of caustic alkalis, glycerol also dissolves ferric oxide, cupric oxide, and bismuth oxide, no doubt in consequence of the formation of soluble compounds (metallic glyceroxides), such as are represented by monosodiumcuproglyceroxide (*see* below). The oxides enumerated above are not reduced to metals, or at most only to their lower oxides. The following oxides: silver oxide (*cp.* above), gold oxide, mercury oxide, rhodium oxide, palladium oxide, and platinum oxide (Ag_2O, Au_2O_3, HgO, RhO_2, PdO, PtO_2), are reduced to metals when heated with alkaline glycerol solution (Bullnheimer).

The great solubility of zinc sulphate, as also of nickel, cobalt and copper sulphates, in glycerol, is explained by the fact that these salts combine with three molecules of glycerol to form compounds (Grün, Ber. 1908, 3465) of the general formula:

$$(M{\cdot}3C_3H_8O_3)SO_4{,}H_2O.$$

For these compounds, the name 'glycerinates' has been proposed by Grün, in order to distinguish them from the metallic glyceroxides described above.

Quantitative Determination of Glycerin.

Here only the determination of glycerol in commercial products containing considerable quantities of it can be considered. The determination of glycerol in wine, beer, and other fermented liquors falls outside the scope of this article (*see* Beer, Wine, &c.). For a full description of the methods employed for the quantitative determination of glycerol, the reader must be referred to Lewkowitsch, Chem. Techn. I. 352.

The methods employed for the determination of glycerol are either direct or indirect methods. A direct method for determining glycerol in oils and fats by isolating it, has been worked out by Shukoff and Schestakoff. It is necessary to operate with a solution containing at least 40 p.c. of glycerol. If the solution be more dilute, a quantity corresponding to about 1 gram of glycerol is carefully evaporated on the water-bath, the concentration not being allowed to reach so high a degree that volatilisation of glycerol can take place (*i.e.* a concentration of about 50 p.c. must not be exceeded). Before evaporating, the solution is rendered slightly alkaline with potassium carbonate. The concentrated solution is then mixed with 20 grams of ignited and powdered anhydrous sodium sulphate and exhausted in a Soxhlet extractor with anhydrous acetone (previously well dried over ignited potassium carbonate). As acetone attacks both cork and indiarubber, all connections must be made with ground-glass fittings. The extraction requires a somewhat lengthy time. Shukoff and Schestakoff directed to extract for 4 hours, but later observers require 5 to 6 and even 9 hours in order to effect complete extraction.

As a rule, the determination of glycerol in oils and fats is carried out by one of the following indirect methods.

Permanganate process. The glycerol solution is made strongly alkaline and a concentrated solution of potassium permanganate is added at the ordinary temperature, until the solution is blackish. The glycerol is converted quantitatively into oxalic acid, carbon dioxide, and water, according to the following equation:

$$C_3H_8O_3+3O_2=C_2H_2O_4+CO_2+3H_2O.$$

This reaction, originally suggested by Wanklyn and Fox, has been worked out as a

quantitative method by Benedikt and Zsigmondy. The excess of permanganate is destroyed by adding a solution of sodium sulphite, and the oxalic acid is determined by precipitating it as calcium oxalate. It is essential that other substances which form oxalic acid on oxidation must be absent. (For a full description of the details of this method, *cf.* Lewkowitsch, Chem. Technol. I. 353.) Other oxidation methods leading to the complete combustion of glycerol, can only be employed in the complete absence of organic impurities.

Acetin process. In case an impure glycerin be under examination (such as the crude glycerins described above), it is most convenient to determine the proportion of glycerol by the Benedikt-Cantor acetin process, which is based on the quantitative conversion of glycerol into triacetin on heating the solution with acetic anhydride. If the product of this reaction is then dissolved in water, and the free acetic acid carefully neutralised with alkali, the dissolved triacetin can be easily estimated by saponifying it with a known volume of standard alkali, and titrating back the excess.

About 1·5 grams of crude glycerin are weighed off accurately, heated with 7–8 c.c. of acetic anhydride and 3 grams of anhydrous sodium acetate (carefully dried in an oven) for 1½ hours in a round-bottomed flask (of about 100 c.c. capacity), connected with an inverted condenser. The mixture is then allowed to cool a little, 50 c.c. of warm water are poured down through the tube of the condenser, and the acetin is made to dissolve by shaking the flask; if necessary, the contents of the flask may be slightly warmed, but must not be boiled. As triacetin is volatile with water vapour, these operations should be carried out while the flask is still connected with the condenser. The solution is next filtered from a flocculent precipitate, containing most of the impurities of the crude glycerin, into a wide-mouthed flask of about 500–600 c.c. capacity, and the filtrate is allowed to cool down to the ordinary temperature. Phenolphthalein is then added, and the free acetic acid neutralised with dilute caustic soda solution. While running this in, the solution must be agitated continually, so that the alkali may not be *locally* in excess longer than is unavoidable. The point of neutrality is reached when the slightly yellowish colour of the solution just changes into reddish-yellow. If the solution is allowed to become pink, the point of neutrality has been exceeded, and a fresh test must be made; the excess of soda cannot be titrated back, as partial saponification of the acetin takes place in presence of the slightest excess of alkali. The change of colour is very characteristic, and is easily recognised after some little practice.

25 c.c. of the strong soda solution are now run in and the solution is boiled for a quarter of an hour; the excess of soda is then titrated back with the standard acid. Side by side, operating in the same manner, 25 c.c. of the strong caustic soda solution are boiled and titrated with acid. The difference between the two titrations corresponds to the amount of alkali required for the saponification of the triacetin. From this, the quantity of glycerol in the sample can be calculated, as shown by the following example: 1·324 grams of a sample have been treated as described above. Let 25 c.c. of the strong soda solution require 60·5 c.c. of normal hydrochloric acid, and let the number of c.c. required for titrating back the excess of soda be 21·5; then 60·5 − 21·5 = 39·0 c.c. have been used. 1 c.c. of normal acid corresponds to 0·092/3 = 0·03067 gram of glycerol. Hence the sample contained 0·03067 × 39 = 1·1960 grams or 90·3 p.c. of glycerol.

The methods best adapted for the examination of the several glycerins or glycerin solutions found in commerce are as follows:—

The proportion of glycerol in *chemically pure glycerin* is best ascertained by determining the sp.gr. (*see* table on p. 768) or by oxidising the glycerol by means of permanganate, provided organic impurities be absent. This is ascertained in the following manner: A somewhat dilute solution is mixed with a cold ammoniacal silver nitrate solution; the solution should remain colourless even after standing for 24 hours. Any acroleïn present in the sample is detected by the test described above. Any polyglycerols, due to faulty distillation, are determined by allowing an accurately weighed quantity of the sample to evaporate gently at 160°. Care should be taken not to heat too rapidly, otherwise even the purest glycerol may become polymerised with the production of the very substances that are to be detected. From the weight of the residue, the weight of ash, subsequently found on incineration, must be deducted. The difference ('the organic residue') is a fair indication of the care with which the glycerol has been manufactured.

The following table gives the 'organic residue' and ash of a number of 'chemically pure glycerins' examined in the author's laboratory; they are arranged according to the amount of organic residue they contain:—

ORGANIC RESIDUE AND ASH IN COMMERCIAL CHEMICALLY PURE GLYCERINS.

(Lewkowitsch.)

No.	Residue at 160° p.c.	Ash p.c.	Organic residue p.c.
1	0·03033	0·00603	0·0243
2	0·0276	0·0030	0·0246
3	0·0377	0·0050	0·0327
4	0·0498	0·0138	0·0360
5	0·0452	0·0081	0·0371
6	0·0509	0·0066	0·0443
7	0·0656	0·0139	0·0517
8	0·0748	0·4000	0·0738
9	0·0905	0·0154	0·0751
10	0·1047	0·0190	0·0857
11	0·1236	0·0305	0·0931
12	0·1621	0·0183	0·1438
13	0·8060	0·2090	0·5970

From this table, rules for the valuation of commercial chemically pure glycerins may be derived. The first six samples certainly deserve the name of chemically pure glycerin, the following four samples represent lower qualities unfit for pharmaceutical purposes, whereas the last two samples are merely glycerins, refined by distillation; the last sample would be rejected as unsuitable even by dynamite makers. Sample No. 2 represents a chemically pure glycerin, manufactured by the author on a large scale from soap-lye glycerin, in 1890 (*cp.* Lewkowitsch,

Year-Book of Pharmacy, 1890, 382; *cp.* also Thorpe, J. Soc. Chem. Ind. 1895, 720).

Chemically pure glycerin must further be free from all but the most minute traces of arsenic. This is ascertained by a modification of Gutzeit's test (*cp.* Lewkowitsch, iii. 332), substituting mercuric chloride for silver nitrate.

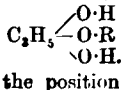
Distilled glycerin (dynamite glycerin). The proportion of glycerol in these products is best determined by the acetin method. 'Dynamite glycerin' is usually sold according to a specification agreed upon between buyer and seller. The following conditions are usually stipulated: sp.gr. not below 1·261; absence of lime, magnesia and alumina; absence of more than traces of chlorine and of arsenic; amount of organic impurities, and total residue not to exceed a fixed quantity. In addition thereto, the 'nitration and separation' tests must be satisfactory. With regard to the details of these tests and the manner of carrying them out, *cp.* Lewkowitsch, Chem. Technol. iii. 306–319.

The determination of the amount of glycerol in all *crude glycerins*, is best carried out by the acetin process (*see* above). For details and special precautions to be observed in the examination of the several crude glycerins, *cp.* Lewkowitsch, Chem. Technol. iii. 301–315 and Report of an International Committee on the Analysis of Crude Glycerin, Journ. Soc. Chem. Ind., 1911, 556.

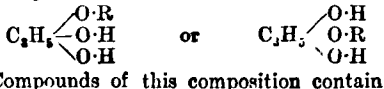
Esters of Glycerol.

The most important esters of glycerol are those resulting from the combination of one molecule of glycerol with three molecules of fatty acids. These esters occur in largest quantities in the natural oils and fats which represent a mixture of a number of simple and mixed triglycerides (*see* Oils, Fixed, and Fats).

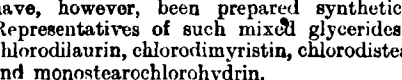
Glycerol, being a trihydric alcohol, is able to form mono-acid and di-acid esters, which are usually described as monoglycerides and diglycerides (although these terms must be considered incorrect, for the term 'monoglyceride' should more appropriately be applied to a triglyceride containing one and the same acid radicle, and the term 'diglyceride' to a triglyceride containing two different acid radicles). The *monoglycerides* have the general formula:



According to the position which the fatty acid radicle occupies in the molecule, two isomeric glycerides may exist, as is explained by the following two formulæ, in which R denotes the fatty acid radicle:—

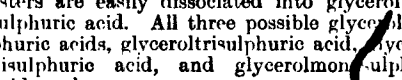


Compounds of this composition contain an asymmetric carbon atom, and may therefore represent racemic compounds. Monoglycerides corresponding to the first formula are termed α-monoglycerides, and those corresponding to the second formula are termed β-monoglycerides. If a second acid radicle enters, the so-called diglycerides are obtained. Theoretically, two isomeric diglycerides containing the same fatty acid radicle are possible, as is indicated by the following two formulæ:



The compounds conforming to the first formula are denoted αα (or symmetric) glycerides; they are prepared from αα-dichlorohydrin and the salts of fatty acids. The compounds corresponding to the latter formula are termed αβ (or unsymmetric) glycerides; they are prepared in a corresponding manner from β-dibromohydrin. αβ glycerides contain an asymmetric carbon atom; hence the synthetically prepared αβ diglycerides are likely to represent racemic compounds. If one or both of the acid radicles were optically active (*e.g.* if derived from ricinoleic, chaulmoogric, or hydnocarpic acid), the diglycerides would be optically active on that account alone.

If the two fatty acid radicles are different, the existence of diglycerides having the following formulæ is theoretically possible:—



These diglycerides may be termed 'mixed diglycerides.' As they all contain an asymmetric carbon atom they may represent racemic compounds. If one or both acid radicles be derived from optically active fatty acids, the diglycerides containing them will exhibit optical activity.

The monoglycerides and diglycerides do not occur in nature, but very strong evidence has been adduced that these esters are formed in the course of slow hydrolysis of the natural triglycerides; hence they may be found in fats and oils which have become rancid by a natural process on exposure to air, light, and moisture.

Glycerol also forms esters with inorganic acids, such as sulphuric, nitric, phosphoric, boric, and arsenious acids.

A mixed triglyceride, containing two acid radicles of fatty acids and one of phosphoric acid, occurs in nature as *Lecithin*, in which two fatty acid radicles and one acid radicle of phosphoric acid are combined with the glycerol rest. In the phosphoric acid radicle, one of the two free OH groups is combined with the base choline. Lecithin appears to be a representative of a whole group of mixed triglycerides (occurring in the liver, in the brain, &c.), which have been termed by Thudichum, phosphatides, and more recently by Leathes, phospholipines.

Mixed triglycerides containing, in addition to one or two fatty acid radicles, two or one radicles of inorganic acids other than phosphoric acid have not been met with in nature; they have, however, been prepared synthetically. Representatives of such mixed glycerides are chlorodilaurin, chlorodimyristin, chlorodistearin, and monostearochlorohydrin.

The sulphuric acid esters of glycerol are obtained by dissolving glycerol in concentrated sulphuric acid. On boiling with steam, the esters are easily dissociated into glycerol and sulphuric acid. All three possible glycerol sulphuric acids, glyceroltrisulphuric acid, glyceroldisulphuric acid, and glycerolmonosulphuric acid are known.

Glycerylphosphoric esters are obtained by heating phosphoric acid with glycerol. The most important ester, commercially, is monoglycerolphosphoric acid, which forms a series of salts (sodium, lithium, calcium, strontium, iron, &c.), largely used in pharmaceutical practice (especially in France).

Of great commercial importance are the nitric esters of which the most important is glyceryl trinitrate, or 'nitroglycerin,' prepared by allowing glycerin to run into a mixture of one part of strongest nitric acid and two parts (by weight) of concentrated sulphuric acid. Nitroglycerin is a heavy oily liquid of sp.gr. 1·60, which volatilises at 160° under a pressure of 15 mm. Its most remarkable property of exploding violently under certain conditions is made use of in high explosives and 'smokeless powders,' such as 'dynamite,' 'blasting gelatin,' 'gelignite,' &c. Glycerin dinitrate $C_3H_5(ONO_2)_2(OH)$, is also used in the manufacture of explosives (*v.* EXPLOSIVES).

Glyceryl arsenite is formed by dissolving arsenious oxide in glycerol and heating to 250°. Above 250° it decomposes. It is volatile with the vapours of glycerol, hence, when distilling glycerin in a current of superheated steam (see above), the arsenite is either volatilised unchanged, or is hydrolysed by the steam; at any rate the distillate contains arsenious acid. Glyceryl arsenite is used in calico printing.

POLYGLYCEROLS.

When glycerol is heated rapidly, polyglycerols are obtained. They are formed by the combination of several molecules of glycerol with loss of water: hence they are formed on a large scale during the distillation of glycerin, when the bulk of the polyglycerols remains behind in the still. The condensation of glycerol to polyglycerol has been effected by Lourenço, by heating glycerol with monochlorohydrin. (For the application of polyglycerols in the arts, *see* above.) J. L.

GLYCEROLPHOSPHORIC ACID and **GLYCEROLPHOSPHATES** *v.* GLYCERIN (GLYCEROL).

GLYCIN is the trade name for the chloride of *p*-hydroxyphenylaminoacetic acid. It is used in photography as a developer (also *v.* GLYCINE).

GLYCINE. *Glycin, Glycocine, Glycocoll, Aminoacetic acid*

$$NH_2{\cdot}CH_2{\cdot}COOH \text{ or } \begin{matrix} CH_2—NH_2 \\ | \quad\quad | \\ CO—O \end{matrix}$$

(Sakurai, Chem. Soc. Proc. 1894, 90; 1896, 38; Walker, Chem. Soc. Proc. 1894, 94). Glycine was discovered in 1820 by Braconnot (Ann. Chim. Phys. [2] 13, 114) among the products obtained by decomposing glue with sulphuric acid. It is obtained by decomposing various protein substances with sulphuric acid (Spiro, Zeitsch. physiol. Chem. 28, 187), and is present as the chief amino-acid in the sugar cane (Shorey, J. Amer. Chem. Soc. 1897, 881; 1898, 137). It may be prepared by treating bromacetic or chloracetic acids with ammonia (Perkin and Duppa, Annalen, 108, 112; Kraut, Ber. 1890, 2577; Mauthner and Suida, Monatsh. 11, 374; Goldberg, Kunz and Kraut, Annalen, 266, 295); by treating chloracetic acid with ammonium carbonate (Nencki, Ber. 1883, 2828); by passing cyanogen into boiling hydriodic acid (sp.gr. 1·96) (Emmerling, Ber. 1873, 1361); by heating potassium phthalimide with ethyl chloracetate (Gabriel and Kroseberg, *ibid.* 1889, 427); by treating nitrosomalonic ester with zinc and acetic acid (Conrad and Schulze, *ibid.* 1909, 729); by boiling hippuric acid with strong sulphuric acid (Curtius, J. pr. Chem. [2] 26, 145; Dessaignes, Annalen, 58, 322); by treating glyoxylic acid with ammonium carbonate and subsequently heating to 120° with hydrochloric acid (Erlenmeyer, junr., and Kunlin, Ber. 1902, 2438); by the action of hexamethylene amine on potassium monochloracetate (Bourcet, Bull. Soc. chim. 19, [3] 1005; Auger, *ibid.* 21, [3] 5). In order to obtain the pure acid, the solution containing the acid, prepared by any of the above methods, is freed from ammonia (if present) and freshly precipitated copper hydroxide is added. The copper salt of the acid crystallises out; this is filtered off and decomposed with sulphuretted hydrogen. Another method consists in extracting the acid with glycerol and thus separating it from the impurities present (Farbw. Meister, Lucius and Bruning, D. R. P. 141976; Zeitsch. angew. Chem. 1903, 16, 527). Siegfried (D. R. P. 188005; Chem. Zentr. 1907, ii. 1466) adds barium or strontium hydroxides to the solution, passes in carbon dioxide, filters off the separated solid and heats it with water.

Properties.—Glycine crystallises in colourless monoclinic crystals, which, when heated, darken at 228°, and melt with the evolution of gas at 232°–236°; sp.gr. 1·1607 (Curtius, *l.c.*). It is soluble in 4·3 parts of cold water and in 930 parts of ethyl alcohol (sp.gr. 0·828), but is insoluble in absolute alcohol. Hydriodic acid reduces glycine to ammonia and acetic acid (Kwisda, Monatsh. 12, 419), whilst sodium amalgam yields amino-acetaldehyde (Neuberg, Ber. 1908, 956; Fischer, *ibid.* 1019). On electrolysis, the acid or the copper salt yields ethylenediamine (Lilienfeld, D. R. P. 147943; Chem. Zentr. 1904, i. 133; Kühling, Ber. 1905, 1638; 1907, 757). Hydrogen peroxide oxidises glycine to glyoxylic acid and formaldehyde (Dakin, J. Biol. Chem. 1, 171): treatment with nitrosyl chloride results in the formation of chloracetic acid (Tilden and Forster, Chem. Soc. Trans. 1895, 491). Glycine and its derivatives are used in photography as developers, in place of pyrogallol, &c. (Farbw. Meister, Lucius and Bruning, D. R. P. 142489; U. S. Pat. 767815; Eng. Pat. 20377; J. Soc. Chem. Ind. 1903, 380), and also for reducing silver images.

Derivatives.—*Aromatic glycines* are prepared from aromatic amines and monohalogenated acetic acids or dihalogenated vinyl ethers (Imbert and Consortium fur Elektrochemiche Industrie, Chem. Soc. Abstr. 1908, i. 975; D. R. P. 199624). *Glycocollamide* is produced when glycocoll and alcoholic ammonia are heated together at 160°. *Glycocollanilide* is prepared from chloro- or bromo- acetanilide and ammonia (Majert, Eng. Pat. 5269; D. R. P. 59121; J. Soc. Chem. Ind. 1892, 369). The *Ethyl ester* is prepared by the action of ammonia on chloracetic acid, and subsequent treatment of the crude dry product with absolute alcohol and dry hydrogen chloride (Hantzsch and Metcalf, Ber.

1896, 1684; Hantzsch and Silberrad, *ibid.* 1900, 70) or by the interaction of hexamethylene amine and chloracetic acid and subsequent treatment as above (Auger, Bull. Soc. chim. [3] 21, 5). It boils at 51·5°–52·5° (10 mm.), and has sp.gr. 1·0358 11·8°/4° (Schmidt, Ber. 1905, 200).

Methylglycine v. SARCOSINE.

Trimethylglycine v. BETAINE.

Glycine anhydride $CH_2<\begin{matrix}NH.CO\\CO.NH\end{matrix}>CH_2$ was discovered by Curtius (J. pr. Chem. [2] 37, 173). It separates out from an aqueous solution of glycine ester on long standing. It is best prepared by treating the hydrochloride of the ester with caustic soda (Fischer, Ber. 1906, 2893). It is a white crystalline solid, which, on heating, becomes brown at 245° and melts at 275°.

Glycocollaminocarboxylic acid esters (*v.* Einhorn, Chem. Zentr. 1901, i. 1115; *D. R. P.* 108027).

GLYCOCOLL *v.* GLYCINE.

GLYCOGEN *v.* CARBOHYDRATES.

GLYCOLLIC ACID, *Hydroxyacetic acid* $CH_2(OH)COOH$.

It is present as the chief acid constituent in the juice from the sugar cane (Shorey, J. Amer. Chem. Soc. 1899, 21, i. 45) and is found in the calcium precipitate formed in the treatment of beet-juice (Lippmann, Ber. 1891, 3299). It is formed by the oxidation of glycol (Würtz, Annalen, 103, 366); by treating alcohol with nitric acid in the cold (Drechsel, *ibid.* 127, 150); by reducing oxalic acid with zinc (Forcrand, Bull. Soc. chim. [ii.] 39, 310); by the electrolytic reduction of oxalic acid in dilute hydrochloric or sulphuric acids, using lead electrodes (Roessler and Hasslacher Chem. Co., U. S. Pat. 837083; D. R. PP. 194038, 204787; J. Soc. Chem. Ind. 1907, 157; 1909, 108; Rainhold, Fr. Pat. 378276; J. Soc. Chem. Ind. 1907, 1097; Avery and Dales, Ber. 1899, 2236); and by treating formaldehyde with equivalent quantities of potassium cyanide and calcium chloride (Kohn, Monatsh. 1899, 903). Glycollic acid may be prepared by boiling a concentrated solution of potassium chloracetate for 24–30 hours in a flask under a reflux apparatus. The product is then distilled under reduced pressure, the temperature being kept below 70°. The residue is mixed with a large quantity of acetone, the solution filtered from the separated potassium chloride, and after a short time the glycollic acid separates from the acetone solution in colourless crystals. The yield is about 85 p.c. (Colman, Chem. Soc. Proc. 1892, 72).

Glycollic acid crystallises from water in crystals belonging to the monoclinic system and from acetone in those of the orthorhombic system (Colman, *l.c.*); m.p. 78·9° (Drechsel, *l.c.*). On heating to 100°, glycollic anhydride $C_4H_6O_5$ is formed, and by heating the calcium salt with much sulphuric acid, metaformaldehyde is produced. Oxidation with nitric acid yields oxalic acid, and reduction with zinc and sulphuric acid results in the formation of acetic acid (Claus, Annalen, 145, 256). It may be detected by heating 0·02–0·1 gram of the substance with 0·2 c.c. of water and 2 c.c. of sulphuric acid (sp.gr. 1·84): after gas has ceased to be evolved, the addition of one drop of *p*-cresol gives a green colouration, or one drop of codeine solution, a yellow colouration changing to deep violet (Denigès, Bull. Soc. chim. 1909, 5, 647).

The glycollates of the alkalis are deliquescent; calcium glycollate $(C_2H_3O_3)_2Ca$ (with 3 or $4\frac{1}{2}$ H_2O) and silver glycollate $C_2H_3O_3Ag,\frac{1}{2}H_2O$ are sparingly soluble in water.

GLYCOSAL. Trade name for a combination of glycerol and salicylic acid introduced as a substitute for other salicylates (*v.* SYNTHETIC DRUGS).

GLYCYPHYLLIN *v.* GLUCOSIDES.

GLYCYRRHETIN, GLYCYRRHIZIC ACID, GLYCYRRHIZIN *v.* LIQUORICE.

GLYOXYLIC ACID $CHO{\cdot}CO_2H$ or $CH(OH)_2CO_2H$.

Found in very young beet-roots (Lippmann, Ber. 1891, 3305), in grapes, unripe apples, plums, gooseberries, currants, and rhubarb (Brunner and Chaud, Ber. 1886, 595; Bull. Soc. chim. [3] 13, 126). Prepared by oxidising alcohol (Debus, Annalen, 100, 1; Boettinger, Arch. Pharm. 232, 65), glycol (Debus, Annalen, 110, 316) or glycerol (Heintz, *ibid.* 152, 325) with nitric acid; by heating ethyldichloracetate with water at 120° (Fischer and Geuther, J. 1864, 316); by exactly neutralising dichloracetic acid with potassium hydroxide (1 : 1) and heating with solid potassium acetate in a reflux apparatus for an hour, filtering the liquid and boiling the filtrate for several hours (Doebner, Annalen, 311, 129); by heating the silver salt of dibrom- or dichloracetic acid with water (Debus, Zeitsch. Chem. 1866, 188; Perkin and Duppa, Annalen, 112, 24; Zeitsch. Chem. 1868, 424; Beckurts and Otto, Ber. 1881, 581); by heating one part of dibromacetic acid with 10 parts of water for 24 hours at 135°–140° (Grimaux, Bull. Soc. chim. [ii.] 26, 483); by reducing the esters of oxalic acid with sodium amalgam (Bayer & Co. D. R. P. 201895; J. Soc. Chem. Ind. 1908, 1176); by the electrolytic reduction of oxalic acid, its esters or its amide in sulphuric acid at a low temperature (Tafel and Friedrichs, Ber. 1904, 3187; Wohl and Lange, *ibid.* 1908, 3614; Kinzlberger & Co. D. R. PP. 163842, 210693; J. Soc. Chem. Ind. 1906, 392; 1909, 815).

Glyoxylic acid is a thick liquid, readily soluble in water, and crystallises in rhombic prisms by long standing over sulphuric acid (Debus, Chem. Soc. Trans. 1904, 1382); the crystals have the formula $C_2H_4O_4$ (Perkin, Ber. 1875, 188). It is a tautomeric substance; it exhibits aldehydic properties in condensing with hydroxylamine, phenylhydrazine, and semicarbazide (Elbers, Annalen, 227, 353; Fischer, Ber. 1884, 576; Simon and Chavanne, Compt. rend. 143, 904), but most of its salts are of the type $(HO)_2CH{\cdot}CO_2M$, whilst dialkyl ethers of the type $(RO)_2{\cdot}CH{\cdot}CO_2H$ have been prepared. Reduction with zinc in aqueous solution yields glycollic acid; in acetic solution, tartaric acid (Genvresse, Compt. rend. 114, 555): nitric acid oxidises it to oxalic acid, whilst potash simultaneously oxidises and reduces it with the formation of glycollic and oxalic acids: treatment with ammonia and subsequent hydrolysis yields formic acid and glycine (Erlenmeyer and Kunlin, Ber. 1902, 2438). With hydrogen cyanide, it forms a cyanhydrin which, on hydrolysis, yields tartronic acid. By warming

with resorcinol and a little absolute alcohol, diluting and adding a few drops of ammonia, a deep blue colouration is produced, rapidly changing to red (Boettinger, Arch. Pharm. 232, 1); sulphuric acid gives a blue or violet colouration with glyoxylic acid (Hopkins and Cole, Proc. Roy. Soc. 68, 21). It condenses with carbamide to form allantoin and with guanidine to form in the cold glyoxylic guanidide and on warming to 100°, iminoallantoin (Doebner and Gärtner, Annalen, 315, 1; 317, 157; Simon and Chavanne, Compt. rend. 143, 51; Kaess and Gruszkiewicz, Ber. 1902, 3604). For other condensations *v.* Boettinger, Arch. Pharm. 232, 549, 704; 233, 100, 199; Bougault, Compt. rend. 148, 1270. For salts *v.* Debus, Chem. Soc. Trans. 1904, 1382. Glyoxylic acid acts as a hydrolysing agent towards cane sugar and starch, and prevents fermentation of products thus formed as it acts on yeast as a poison (Boettinger, Arch. Pharm. 233, 287; Bouveault, Bull. Soc. chim. [iii.] 19, 78). For physiological action in the body, *v.* Eppinger, Beitr. chem. Physiol. Path. 6, 492; Almagia, *ibid.* 7, 459; Schloss, *ibid.* 8, 445; Granström, *ibid.* 11, 132; Dakin, J. Biol. Chem. 1, 271; Hofbauer, Zeitsch. physiol. Chem. 52, 425; Adler, Arch. exp. Path. Pharm. 46, 207.

GOA POWDER *v.* ARAROBA POWDER.

GOLD. Sym. Au (Aurum). At.wt. 197·2.

Historical.—Gold cannot have escaped the observation of the men of the Stone Age, but it could have been of little use to them except for ornamentation until they had discovered the art of melting. Flint daggers with gilt handles have been found in Egypt, and gold was well known in that country about 3600 B.C., when its value in relation to silver was fixed by law. It was first used for coinage in Lydia, about 700 B.C. in the form of electrum, a native alloy of gold and silver.

The earliest method of obtaining gold, other than that of collecting it by hand, was by washing with water on sloping rocks. Sheepskins were spread out for entangling the particles of metal and helping in its collection. Over 2000 years ago, the methods of ore-crushing by hammers and also by means of pestles and mortars were adopted in Egypt to release gold contained in solid rock. The powdered ore was washed on sloping tables. The use of sieves is also attributed to the Egyptians. Heavy pestles or stampers, requiring water power or the united efforts of several men to raise them, were not employed until much later. Stamp batteries for crushing ore were established at Joachimsthal in 1519, and sieves set at the outlet of the mortars were described by Agricola in 1556 and were seen by Jars in the Hartz in 1767.

The use of mercury for separating gold from other materials by amalgamation was described by Pliny and referred to by Theophilus in the 11th century in his description of the extraction of gold from the sands of the Rhine. The method used in the Tyrol of stirring crushed ore with large quantities of mercury in circular bowls is of great antiquity, but the practice of charging mercury together with uncrushed ore into the mortars of stamp batteries and catching the gold amalgam on copper plates was not mentioned before 1850.

The chlorination process of gold ore treatment originated in 1848, and the cyanide process was invented by MacArthur and Forrest in 1887. The methods of refining gold by the cementation process and by cupellation are very ancient. Nitric acid for refining was in use in Venice in the 15th century and was not superseded by sulphuric acid until the 19th century. The electrolytic refining process, invented in 1888, has now replaced the sulphuric acid process in America.

Gold ores. Gold is widely distributed in nature. It occurs in minute traces in all ores of silver, copper, lead, antimony, and bismuth. It has been detected in igneous and metamorphic rocks in almost every case in which a careful search for it has been made, and sedimentary rocks are seldom quite free from it. The comparatively small quantities of gold in limestones which have been formed in clear water far from land, appear to indicate the land as the place of origin of the gold, but it is also present in sea water.

Gold occurs in quantities large enough to pay for extraction in many quartz veins or lodes in rock formations. The gold is disseminated in the quartz and is accompanied by brown oxides of iron in the upper portions of the deposits and by sulphides in the deep-seated portions. It usually occurs as native gold and even when it is contained in pyrites or other sulphides, it is present in the free state. Native gold also occurs in many secondary or detrital ('placer') deposits, such as river gravels, sea beaches, &c., in the form of nuggets, grains, and flakes. The auriferous beds of conglomerate in the Transvaal are of this character.

Native gold occurs in the form of rounded, irregularly shaped nuggets, pellets, grains, &c., which show crystalline structure when polished and etched but rarely exhibit regular crystal faces or angles externally. It always contains some silver and copper, and other metals are also generally present in smaller proportions.

Telluride of gold is found in large quantities in Western Australia, Colorado, and Transylvania, and has been reported from many other localities. There is only one true compound of gold and tellurium, which corresponds with the formula $AuTe_2$, and contains 43·6 p.c. of gold; but several compounds consisting of various mixtures of tellurium with gold and silver and other metals have been recognised as mineral species. The best known of these are (1) *calaverite*, which has the composition $AuTe_2$, (2) *sylvanite* or graphic tellurium which appears to be a variable mixture of $AuTe_2$ and Ag_3Te_4, (3) *petzite*, a telluride of silver, Ag_2Te, with part of the silver replaced by gold, and (4) *nagyagite* or foliated tellurium, which contains some lead.

Auriferous telluride is usually dark grey or black in colour, but occasionally is silver-grey. Sometimes it contains an admixture of metallic gold which gives it a brassy-yellow colour. It is soft and brittle but its density is high, usually between 8 and 9. When heated in air, it oxidises, fuming and giving off TeO_2, and fuses below a red heat. If the roasting process is continued, most of the tellurium is removed and the gold is left in the form of spherical pellets which have solidified from fusion. Calaverite may contain as much as 44 p.c. of gold, but

part of this is usually replaced by silver. A specimen of sylvanite from Cripple Creek, Colorado, contained gold 7·64 p.c., silver 32·39 p.c., tellurium 59·96 p.c. (F. C. Smith), and a specimen of petzite from California contained 25·6 p.c. of gold and 41·86 p.c. of silver.

Extraction of gold from its ores. The metallurgical treatment of gold ores is usually simple and cheap and owing to this circumstance and to the high value of the metal, ores containing very small proportions of gold can be worked at a profit. Thus the ores of the Witwatersrand, now being worked, contain, on an average, only about 6 or 7 dwt. of gold per ton, or little more than 0·001 p.c., and in the case of auriferous gravel a ton rarely contains more than a few grains of gold.

Washing auriferous gravel.—The gold occurring in placers is obtained by washing away, with the aid of water, the lighter gravel from the gold disseminated through it. A large number of appliances and machines are in use for this purpose. Generally the larger stones are removed by some form of sieve and the finer material is carried by a shallow stream of water through inclined troughs ('sluice-boxes') or over sloping tables. The heavy particles of gold sink to the bottom of the stream and are caught by the rough surface of blanketing or plush or in crevices which are formed by the supply of 'riffles' of various kinds. Sometimes the riffles consist of wooden strips or poles, sometimes of iron rails or sheets of 'expanded' metal. Mercury is sprinkled in the stream and accumulates in the crevices, where it assists in catching the gold by amalgamating with it. The gold-amalgam, recovered in the periodical 'clean-up,' is strained through canvas to remove the excess of mercury and afterwards retorted.

The gravel is mined in various ways, according to circumstances. It may be raised by the spade and thrown into the stream, or when in high banks it may be broken down and washed away by jets of water ('hydraulic mining'). Gravels cemented by infiltration are crushed before being washed. Of late years, dredgers have been largely used, originally to recover the gravel from river beds and more recently on dry alluvial 'flats.' In the latter case, the dredger floats in a pond, and travels slowly across country, scooping away the ground in front and stacking it behind after it has been washed. Placer mining is now of less relative importance than formerly owing to the exhaustion of many of the known deposits.

Stamp battery.—Auriferous quartz is treated, wherever it is possible, by crushing in stamp batteries and amalgamation. The residue or tailing is subsequently treated in various ways, especially by the cyanide process.

Stamps are heavy iron or steel pestles which are lifted and let fall in iron mortars. They have gradually increased in weight, the 50 lb. stamps of 100 years ago having become the 900 lb. stamps of the nineties and the 1·00 or 2000 lb. stamps which have been installed in the Transvaal. The height of drop is usually about 7 or 8 inches and the number of drops per minute about 100. Water and ore are fed into the mortar continually and the fall of the stamps splashes the mixture against a wire screen or perforated metal plate set in the side of the mortar. The finely comminuted material passes through the screen and usually falls directly upon gently sloping amalgamated copper plates. Sometimes mercury is fed into the battery with the ore and amalgamated plates are fastened to the inside of the mortar, but these practices are becoming less common and are impossible with modern heavy stamps. It is now considered advantageous to remove the amalgamated plates to another building at some distance from the stamp battery in order to avoid excessive vibration.

The pulp from the battery is often further reduced in size by passing through a tube-mill, a revolving cylinder half-filled with pebbles, and in that case a coarser mesh is used in the battery screens. Shaking amalgamated plates are placed at the outlets of the tube-mills, and the ordinary amalgamated plates between the battery and the tube-mills are sometimes omitted.

Other machines are occasionally used for fine grinding, as, for example, amalgamating pans (*see* article SILVER for description of these machines). Roller mills, such as the Huntington mill, are sometimes used instead of stamps for crushing soft or brittle ores, or as intermediate grinders. In the Huntington mill, four rollers with vertical axes run around in an iron pan, and are pressed against its periphery by centrifugal force. Chilean mills, which resemble mortar mills, are also used for crushing ore, and for intermediate grinding, being placed between coarse crushers and fine grinders. Some ores are crushed dry, for example those which require to be roasted before treatment. This is done in stamp mills, in certain roller mills, by crushing rollers (where the ore passes between two revolving rollers) and in ball mills, in which iron or steel balls fall from shelf to shelf inside revolving cylinders.

In some of the most modern gold extraction works in the Transvaal, the ore is broken to a maximum size of about 1¼ inch in rock-breakers of the reciprocating type in which the jaws alternately advance and recede. Gyratory rock crushers are also used. The ore is then passed to the stamp battery and crushed by heavy stamps through coarse screens containing in some cases only 9 holes to the square inch. The size of the aperture is here 0·27 inch, the maximum dimensions of ore which can be advantageously treated in tube-mills. Under these conditions, the amount of ore crushed per stamp per day is as much as 20 tons against 4 or 5 tons in adjoining mills where lighter stamps and finer sieves are used. Such coarse material as that indicated above cannot be passed over amalgamated plates, as these would be scoured free from mercury, &c., and it is accordingly passed direct to (inverted) cone classifiers, where the coarse particles settle in water and are retained, whilst the fine material is carried away in the overflow, and sent to the cyanide works. A diaphragm guards the axis of the cone so that the settlement of the sands takes place round the periphery. The underflow or discharge from the apex of the cone, containing the coarse material, including all the coarse free gold, is fed into tube-mills together with some of the water from the overflow. On issuing from the tube-mill, the pulp, which now contains only a small

proportion of material too coarse to pass through a 60-mesh sieve (aperture 0·008 inch), is slightly diluted with water and then passed over shaking amalgamated plates where the coarse free gold is extracted. The tailing from the shaking plates is discharged into the stream of pulp coming from the battery and again passes to the cone classifiers, the oversize being thus returned to the tube-mill. The material passing through the tube-mill contains much less water (say 2 parts of water to 1 of ore) than that coming from the battery and that going to the cyanide works. The last-named pulp is in a very finely divided state and contains no coarse free gold. It is thus in a suitable condition for treatment by cyanide.

Classifiers other than simple cones are also in use in various parts of the world, such as the Dorr classifier in North America and their work is assisted in some mills by concentrators such as Wilfley tables. The sulphide obtained by concentration is usually rich in gold and is treated either by cyaniding, by chlorination, or by smelting with lead ore. Formerly such material was, in many cases, ground with mercury in pans, but this method is now somewhat old-fashioned.

Amalgamation depends on the property possessed by mercury of 'wetting' gold when brought in contact with it. In battery amalgamation, the crushed pulp flows in a thin stream over sloping tables covered with sheet copper, the surface of which has been amalgamated by rubbing with mercury. Particles of gold, silver, or amalgam, on coming in contact with the amalgamated surface adhere to it and so the plate becomes covered with amalgam of the precious metals. In order to increase the chances of contact between the gold and the plates, little falls or steps down of 2 or 3 inches in height are sometimes made between the upper and lower parts of the inclined tables. It has been found that the catching powers of the plate improve as amalgam of the precious metals accumulate on it and it is accordingly usual to electroplate the copper with silver before amalgamating it or to dress it with silver-amalgam or even with gold-amalgam. The surface is kept bright and untarnished by cleaning with cyanide, and additional mercury is sprinkled on if the amalgam-surface becomes hard and dry from the accumulation of silver and gold. The excess of amalgam is brushed off at intervals and squeezed in canvas bags to separate the surplus mercury. The pasty amalgam retained by the canvas is then retorted and the residue melted with suitable fluxes and cast into bars.

Gold will absorb about six times its weight of mercury, forming a silver-white solid amalgam containing about 13·5 p.c. of gold, but in ore treatment, time does not admit of the complete saturation of the gold with mercury, which slowly penetrates into the solid metal by diffusion. The result is that the gold-amalgam collected in cleaning-up in a gold mill consists of little 'nuggets' of gold immersed in a bath of mercury by which their outside layers are saturated. When the mixture is strained through canvas, the excess mercury passes through carrying some gold in solution and leaving behind most of the gold with its adherent mercury. If the gold is very finely divided, the penetration by mercury is more nearly complete, and the percentage of gold in the solid amalgam smaller than if the particles of gold are comparatively large. The composition of the amalgam is also affected by the extent to which other metals are present, as these also form solid amalgams with mercury and reduce the value of the product. Generally speaking, squeezed amalgam resulting from the treatment of gold ores contains from 20 to 50 p.c. of gold. It may also contain silver, copper, iron, &c., in varying proportions.

One of the difficulties in amalgamation is the 'flouring' or 'sickening' of mercury, due chiefly to the presence of arsenic or certain other impurities in the ores. The mercury is broken up into a number of excessively minute globules which have the appearance of flour, and is then swept away in the stream of ore and water and lost in the tailing. Impure mercury containing lead, zinc, &c., is easily floured, as the base metals oxidise and form a coating over the surface of the globules of mercury, thus preventing them from coalescing. The remedy is to purify the foul mercury by distillation, but in the treatment of certain ores it soon again becomes impure. The violent action of stamps on mercury when it is fed into the mortars also causes its excessive subdivision, and it is now unusual to feed mercury into the mortars, the practice being in any case permissible only with light stamps.

Another difficulty is caused by the discolouration of the copper plates, which become covered by a film of oxide or carbonate, with the result that their catching powers are impaired. The attack on the plates is generally caused by acidity of the water due to oxidation of iron sulphide, &c., in the ore. Sometimes the difficulty has been met by the addition of caustic lime to the ore in order to keep the pulp neutral or alkaline. Stains on the plates are removed by brushing with a solution of potassium cyanide. Plates which have been coated with electro-deposited silver are more easily kept in good condition than others.

The treatment of ore by passing it over amalgamated plates removes only a part of the gold, the percentage varying with the ore. In many cases from 50 to 70 p.c. of the gold can be recovered in this way, very few ores being completely 'free-milling,' *i.e.* yielding all their gold to mercury. Some ores are highly 'refractory,' yielding little when subjected to amalgamation, and these are treated by cyaniding, by the chlorination process or by smelting.

The cyanide process.—The tailing from amalgamation contains some finely divided gold which escapes extraction by mercury but is usually readily soluble in solutions of the cyanides of the alkali metals. The solvent action of cyanide on gold is very slow and requires the presence of an oxidising agent such as free oxygen. It may be expressed by the following equation, which represents the sum of the chemical actions:—

$$4Au+8KCN+O_2+2H_2O=4KAu(CN)_2+4KOH$$

The potassium aurocyanide formed in this way remains dissolved in the water. The oxygen required is dissolved in the cyanide

solutions from the air in contact with it. If the oxygen is exhausted owing, for example, to the cyanide solutions remaining for some time in contact with ore containing readily oxidisable sulphide or organic matter, dissolution of the gold is stopped, and it is necessary to aerate the pulp. Very dilute solutions of cyanide are used, containing from about 0·5 p.c. to as little as 0·001 p.c. of potassium cyanide.

Crushed ore or tailing is treated in large vats (containing as much as 400 tons of ore) with false bottoms provided with filter beds. Cyanide solution is run on to the ore and allowed to percolate through it. Fresh solution is added from time to time and finally the ore is washed with water. The solutions pass through the filter by which they are clarified and are conveyed to the precipitation boxes, where the gold is separated, as described later.

Some ores are not amalgamated before treatment with cyanide. In these cases, it may be advantageous to crush in cyanide solution instead of water, and the method is used at the Black Hills, Dakota, and elsewhere.

There are numerous modifications in the process necessitated by the conditions or introduced as improvements. Of these, the variations in mechanical treatment are the most important and complex. Difficulties in leaching crushed ore are caused by the presence of 'slime' or impalpable particles which render the ore impervious to the passage of liquids, unless it is treated in thin layers. To avoid this difficulty, the crushed ore is divided into sand and slime in 'classifiers,' by taking advantage of the difference in the rate of settlement of the particles in water. The 'sand' consists of the particles which settle readily in water. It is easily leached, liquids passing through it under the action of gravity with great rapidity. It is sometimes separated from the excess of water contained in it ('de-watered') by means of filters, and is treated by simple leaching as indicated above. The 'slime' does not readily settle in water, and cannot be leached directly except under high pressure.

The classification may be effected by merely running the stream of pulp into a large vat filled with water, when the sand settles and fills the vat and the slime is carried off in the overflow. Either the sand is cyanided where it settles or it is drained and transferred to another vat for the purpose, thus becoming well mixed and aërated. Another method of separation is by the use of 'spitzlutten' or pointed troughs, in which a rising current of water carries off the slime, the heavy sand falling through the water and being discharged at the apex of the trough. Cone classifiers and other modern appliances have already been mentioned in connection with tube-mills. Various devices are in use for the even distribution of the sand in filling the treatment vats.

The slime is de-watered by settlement and decantation, often with the aid of dissolved lime (by which the slime is coagulated), and is then agitated with dilute cyanide solutions and washed by decantation in conical vats. Slime is usually aërated by the passage of compressed air which is forced through perforated pipes at the bottom of the vats, thus serving to agitate the pulp at the same time. The addition of about 0·25 p.c. of oxides of manganese and iron to the slimed pulp, and the use of air-agitation on the same charge (Adair-Usher process) has been widely adopted in the Transvaal. An alternative method of treating slime is by means of filter presses, pressure being applied by compressed air or by vacuum pumps. Many forms of filters are in use, both for de-watering and for washing out dissolved gold.

The gold contained in pyrites or other sulphide is less readily soluble than ordinary free gold, owing to the absorption of oxygen by the sulphide. When the sulphide is separated as concentrate by the use of travelling-belt vanners, Wilfley tables, or other machines, this disadvantage becomes serious, and such material, as has been mentioned above, is sometimes shipped to smelting works instead of being treated by cyanidation.

Ores may also contain 'cyanicides' by which potassium cyanide is destroyed as such. Acidity of the ore due to oxidation of sulphide is not uncommon and this is corrected by washing with alkali before the cyanide solution is applied, or by crushing the ore with lime. Certain cupriferous ores destroy so much cyanide that they cannot be treated profitably by the process.

The treatment of telluride ore by cyanide presents great difficulties, as potassium cyanide has little action on telluride of gold. Either the ore must be roasted in order to expel the tellurium before cyaniding, or an addition of bromocyanogen must be made to ordinary KCN. The mixture readily dissolves telluride of gold. If coarse free gold is present in the telluride ore, it is extracted by amalgamation. In Western Australia, the telluride ores, after treatment in various ways, which involve roasting the concentrate or the whole of the ore, regrinding in tube-mills, classification, agitation with cyanide, &c., are almost universally filter-pressed.

Precipitation of gold from cyanide solutions is usually effected by zinc shavings contained in long boxes divided into compartments by means of partitions which force the solution to flow through the zinc upwards and downwards alternately. The zinc is coated with lead by immersing the shavings in a solution of lead acetate, in order to expedite the precipitation, especially in weak solutions. The zinc dissolves in the cyanide solution and gradually wastes away. The gold is precipitated chiefly in the form of black slime. In 'cleaning up,' the zinc is washed free from cyanide and digested in sulphuric acid or sodium disulphate, until all action has ceased. The residue now freed from zinc is washed, filtered, dried, and fused in pots with borax, manganese dioxide, or nitre, and sodium carbonate. After casting, the bullion is separated from the slag and sold to refineries. An alternative method is to smelt the gold-zinc slime with litharge, charcoal, &c., and to cupel the base lead-bullion produced (Tavener process). In some mills, precipitation is effected with zinc-dust which is agitated with the clear cyanide solution. The precipitated gold is separated by filter pressure and is smelted at once without previous acid treatment. Another method of precipitation is by the passage of a current of electricity, using sheet-lead for the cathodes, and iron plates or lead coated with

peroxide of lead for the anodes. The gold is precipitated on the lead, chiefly in black granular form, and is recovered by cupellation.

Chlorination is not now in wide use, having been displaced in great part by the cheaper cyanide process. The ore is roasted in air to oxidise the sulphides, arsenides, protosalts, &c., and is then slightly damped and subjected to the action of chlorine gas in tubs or is treated with a solution of chlorine either in revolving barrels or in large vats. Gold is dissolved as the trichloride, and is subsequently precipitated by ferrous sulphate, sulphuretted hydrogen or charcoal. At the Mount Morgan mine, Queensland, the chlorine solution is run on to the ore which is contained in large vats holding 100 tons each. Fresh chlorine solution is added continuously for 36 hours, and drawn off through the filter bed at the bottom. When the dissolution of the gold is complete, the ore is washed with water, and the solution is heated to expel free chlorine and is then passed through charcoal filters in which the gold is precipitated. The charcoal is burnt in a reverberatory furnace and the ashes melted with fluxes.

Smelting.—Gold ores containing appreciable quantities of lead or copper are usually smelted for the production of these metals, from which the gold is subsequently extracted. Other gold ores are sometimes useful as fluxes in the smelting operations (*see* articles COPPER and LEAD).

Refining. Gold extracted from ores is usually impure and unfit for use in the arts until it has been refined. Preliminary refining or 'toughening' operations are often carried out either at the refineries or at the gold mills before the bullion is sold. Sometimes the gold is melted in crucibles with oxidising agents such as nitre, or a blast of air is directed on the surface of the molten metal or even passed through it. The base metals are oxidised and form a dross which is skimmed off with the help of bone ash, or borax is added to form a fusible slag with the oxides of the metals. In the Transvaal, the gold precipitate obtained in the cyanide process is often refined by cupellation with excess of lead (Tavener process). Toughened bullion contains little except gold, silver, and copper.

In London and on the Continent of Europe, gold bullion is usually refined by 'parting' with sulphuric acid. In this process, an alloy of gold and silver is prepared by melting gold bullion with 'doré' silver (*i.e.* silver containing small quantities of gold) or Mexican dollars or occasionally with refined silver if no other is available. The parting alloy usually contains from 20 to 30 p.c. of gold and a few p.c. of copper. If a higher proportion of gold is present, some silver remains undissolved and is retained by the gold. The copper assists the dissolution of the silver.

The alloy is granulated by being poured into water while still molten and the granulations are boiled in concentrated sulphuric acid of sp.gr. 1·85 in cast-iron kettles. The amount of acid used is four or five times the weight of the granulations, but only about half this amount is added at first. The sulphur dioxide, which is formed in large quantities, is carried away through leaden pipes. Silver sulphate is retained in solution in the hot concentrated acid, but tends to be precipitated when the acid is cooled or diluted. When the evolution of sulphur dioxide is at an end, the liquid is transferred to a settling pot, and fresh acid added. After three boilings in acid, the 'brown gold' residue is washed with boiling water, dried, melted with nitre, and cast into ingots of about 400 ozs. each, in open moulds.

The acid solution of silver is poured into large lead-lined tanks containing hot water and sheet or scrap copper, and is heated by means of steam and stirred until the precipitation of the silver is complete. The silver precipitate is washed, dried, and compressed into cakes by hydraulic power before being melted. The solution is alternately concentrated by evaporation and allowed to cool, successive crops of crystals of copper sulphate being obtained, of which the first is the purest. The gold produced by sulphuric acid parting is usually from 996 to 999 fine, and the precipitated silver is about 996 or 998 fine. Formerly nitric acid was used at Philadelphia as an adjunct to the sulphuric acid process before the introduction of the electrolytic process.

In the United States and in some refineries in London and Germany, gold is refined by electrolysis. Two processes are used successively. In the *Moebius process*, a parting alloy containing not more than 30 p.c. of gold and at least 70 p.c. of silver, copper, lead, &c., is electrolysed in a solution containing about 2 p.c. of free nitric acid and 3 p.c. of silver in the form of nitrate. Silver, copper, and some other metals are dissolved at the anodes, and silver is deposited at the cathodes which consist of rolled sheets of pure silver. The current density is 7·5 amperes per square foot of cathode surface at Philadelphia, and as much as 20 amperes per square foot at Denver. The silver is deposited in a coherent form on the cathodes with the help of a little gelatin in the electrolyte and is subsequently stripped off. The gold remains undissolved at the anodes and retains some silver. The copper, lead, zinc, &c., accumulate in the electrolyte, which is kept in condition by the addition of silver nitrate and by frequent renewal. The gold anodes are sometimes boiled in sulphuric acid, but if they contain as much as 950 parts of gold per 1000, they may be melted at once and cast into anodes for treatment by the Wohlwill process.

In the *Wohlwill process*, the anodes contain not more than 50 parts of silver per 1000 and a few parts per 1000 of base metals. By the use of a 'pulsating' current (a combination of a direct and an alternating current), it is claimed that material containing a greater proportion of silver can be treated, as the silver chloride is automatically detached from the anodes. The electrolyte contains from 2 to 10 p.c. of hydrochloric acid and from 2·5 to 6 p.c. of chloride of gold. It is heated to a temperature of 60° to 70°. The higher strengths are in use at Denver where a high current density of 60 amperes per square foot is used. If the hydrochloric acid is insufficient in amount, or if the electrolyte is not hot enough, or if too high a current density is used, some chlorine is given off at the anodes and a corresponding amount of gold remains undissolved. The anodes are made of such thickness (4 to 12 mm.) that they can be dissolved in from 24 to 36 hours under the conditions of treatment. The cathodes consist of

fine gold and the deposit on them is almost pure gold, so that copper, lead, zinc, tellurium, &c., accumulate in the solution, to which it is necessary to add gold chloride at frequent intervals. The residue at the anodes consists chiefly of silver chloride, but any platinum that may be present remains there and some gold is also left undissolved. The anode mud is boiled in sulphuric acid which converts the AgCl into Ag_2SO_4.

The gold and silver refined by electrolysis are of high quality. They can easily be made over 999 fine and are always free from lead and other deleterious elements which are occasionally left in small quantities in the gold refined by sulphuric acid, rendering it unfit for use in the arts.

Miller process. In Australia, gold is refined by the passage of a stream of chlorine gas through the molten metal, a method invented by Miller in 1867. The chlorine is conveyed through a clay pipe, which is inserted in the metal. Zinc, iron, &c., are chloridised first and are sometimes removed by a current of oxygen before chlorine is passed through. Silver is attacked last, and the end of the operation is recognised by the appearance of a characteristic 'flame,' denoting that the chlorine, which in the earlier stages is completely absorbed, has begun to pass unchanged through the metal. The fused chlorides are baled out into moulds and the refined gold stirred and cast into ingots. The chlorides, which contain from 5 to 10 p.c. of gold, are remelted and small quantities of sodium bicarbonate are added without stirring. Some silver is reduced at the surface of the charge, and falling through the chlorides carries down the gold with it. An alloy is thus produced, containing from 40 to 60 p.c. of gold, which is again passed through the refining process. The slabs of silver chloride are boiled in water to free them from the chlorides of copper, zinc, &c., and the silver is then reduced by means of iron and hydrochloric acid. The refined gold is about 996 fine. The method is inconvenient if a large proportion of silver is present in the bullion to be refined.

Properties of gold. The characteristic yellow colour of gold is made redder by the presence of copper and paler by the presence of silver. In certain proportions the effect of one of the two metals neutralises that of the other. Molten gold is green in colour, and very finely divided gold is usually of some shade of purple, as in the case of gold which has been volatilised and condensed.

Gold is the most extensible of all metals, and can be reduced by hammering to a thickness of 0·00008 mm. Its malleability and ductility are reduced by the presence of impurities, of which bismuth, lead, and tellurium have the most striking effects. Gold, containing 0·25 per 1000 of bismuth, is brittle. The melting-point of pure gold is 1064°, but if 0·2 p.c. of tellurium is contained in it, it softens at 260°, the melting-point of the telluride, $AuTe_2$. The presence of most other metals reduces the melting-point of gold, but platinum raises it and silver does not materially affect it, unless it amounts to at least 30 p.c. of the alloy. The density of cast gold is about 19·3 but that of precipitated gold is higher, varying up to 20·72.

Gold is unaffected by the air at all temperatures and can be melted and solidified without being changed. In large pieces, it is not perceptibly attacked by alkalis or by nitric, sulphuric, or hydrochloric acid, but, when finely divided, it is slightly soluble in boiling HCl and in boiling HNO_3. It is freely soluble in *aqua regia* or other mixtures, evolving one of the halogens, and more slowly by cyanide solutions in the presence of air. Its compounds are generally formed with difficulty and decomposed very easily with the isolation of the metal.

Alloys of gold. The *gold-copper* alloys are harder, more fusible, of higher tensile strength, and less malleable and ductile than pure gold. The metals are miscible in all proportions when molten and on solidification separate only to a slight degree. The first additions of copper to gold cause a rapid lowering of the melting-point, the minimum of 905° being reached at the alloy containing gold 82 p.c., copper 18 p.c. This alloy is somewhat brittle, breaking under the hammer with a conchoidal fracture, and is unsuitable for the manufacture of wares. The densities of the alloys when cast are as follows :—

Proportion of gold	Density
100 p.c.	19·31
91·66 ,,	17·35
90·0 ,,	17·17
75·0 ,,	14·74
58·3 ,,	12·69
25·0 ,,	10·03

When the alloys are rolled or hammered, the densities are higher, and the densities of gold wares, which consist of triple alloys of gold, silver, and copper, are also higher.

Gold-silver alloys are soft, malleable, and ductile and all their properties are intermediate between those of gold and silver. The colour is dominated by the silver, the alloy containing 37·5 p.c. of gold being only just distinguishable in colour from pure silver. Alloys containing not less than 65 p.c. of silver are almost completely parted by boiling nitric or sulphuric acid, the silver being dissolved and the gold left behind as a brown sponge or powder. The gold obstinately retains about 0·1 p.c. of silver, and on continued boiling in strong nitric acid, some gold is dissolved whilst the proportion of silver is reduced very slowly. The presence of copper facilitates the action of the acid but does not alter the final result.

Amalgams or alloys of gold and mercury are formed at ordinary temperatures by direct union of the two metals. Mercury dissolves 0·11 p.c. of gold at 0° and 0·126 p.c. at 100°, and gold absorbs about 6 times its weight of mercury, forming a silver-white solid alloy containing about 13·5 p.c. of gold. At 440° most of the mercury is removed by volatilisation, the residue containing about 75 p.c. of gold. At a bright red heat, almost all the remainder of the mercury is distilled off. In the alternative, the mercury can be removed by dissolving it in nitric acid.

Gold-iron alloys are hard but malleable and ductile. Alloys, containing between 15 and 20 p.c. of iron, are used in jewellery in France under the name *or gris*. Their colour is grey-yellow and they melt at temperatures higher than that of pure gold. *Or bleu* contains 25 p.c. of iron. It melts at a temperature of 1160°.

Gold forms a brittle purple compound with aluminium, containing 21·5 p.c. of aluminium and having the formula $AuAl_2$ assigned to it.

The compound AuZn, containing 25 p.c. of zinc, is of a pale lilac colour and is also brittle. There are many other intermetallic compounds containing gold, usually brittle substances of a silver-white or greyish colour. Zinc removes gold from molten lead, forming the compound $AuZn_8$, and aluminium has the same property, the compound formed being $AuAl_2$.

Uses of gold. Gold is used in the form of its alloys with copper, silver, &c., in the manufacture of coin, plate, and jewellery. Gold leaf is used for gilding by hand and potassium aurocyanide is used in gold plating baths. Gold is also used in photography (in the form of sodium chloro-aurate); in dentistry (as alloys); in medicine (as the chloride); and in the manufacture of mirrors for reflecting purposes. In the form of purple of Cassius, it is used for colouring glasses and glazes. Gold lace consists of excessively fine strips of gold twined round silk and contains about 2·5 p.c. of gold by weight.

Manufacture of coin.—The alloy richest in gold now used in coinage contains 986·1 per 1000 of gold and 13·8 of copper. This is the standard of the Austrian ducat which is not current in Austria but is intended for trade purposes. The standards of 916·6 (British Empire, Turkey, Portugal, &c.) and 900 (most other countries) are used generally for current coin, the exception being Egypt where the standard is 875. The alloy is principally copper, but small quantities of silver are present in most coins, the proportion being higher in old ones. Fine gold was used for coinage for a time in Ancient Greece and also in Rome, under the Republic, but copper was afterwards added to reduce the cost. Fine gold is still used for some medals. It is now universally admitted that the alloy with copper is better than pure gold for coinage, owing to its lower melting-point, which is advantageous in the manufacture, and its greater hardness, which enables it to resist defacement better and perhaps to be less readily abraded. The only disadvantages of the alloy with copper are that it blackens when heated and is made brittle by the presence of a minute proportion of lead or tellurium. Fine gold is not affected until the proportion of lead is five or six times as high (0·15 p.c. as against 0·025 p.c.).

In the manufacture of coin, refined gold is melted with copper in graphite crucibles and cast into bars in upright (closed) iron moulds. Charges of about 2500 ozs. are used at the Royal Mint and the fuel is ordinary illuminating gas with a blast of air. Naphtha gas or oil are in use at some other mints, but solid fuel has now been discarded generally. The loss of gold in melting is about 0·2 per 1000, about half of which is volatilised and can be recovered by the use of suitable condensing chambers. The remainder is in the 'mint sweep.'

After being assayed, the gold bars are rolled down, blanks or discs are cut out by punches, and the blanks annealed in gas furnaces, air being excluded. The blank is placed in a collar and struck between dies by means of a lever press. A single blow suffices for the production of each coin, the design on each side being impressed simultaneously, while the metal is forced laterally by the pressure into the corrugations of the collar. Finally, the coins are weighed singly on automatic balances which reject those outside the limits of weight allowed by law.

Gold wares.—The alloys used in the manufacture of gold wares consist of gold, silver, and copper. The wares are usually made from rolled plates which are cut out by punches and struck between dies. The pieces are fitted together by hand, usually by means of soldering. Solders generally contain less gold than the parts which have to be joined together. Decorative work is carried out by hand-hammering, engraving, chasing, &c. The wares are 'coloured' or pickled by a process which removes the silver and copper from the surface and leaves a coating of pure gold, afterwards burnished. In pickling, the wares are heated to redness in air and the blackened surface is removed by boiling in dilute sulphuric or nitric acid, after which the colour is improved by immersion in hot mixtures of nitre, common salt, alum, &c. The standards of gold wares authorised by law in the United Kingdom are 22-carat (*i.e.* containing 22 parts of gold out of 24) 18-, 15-, 12-, and 9-carat. Other standards are in use abroad.

Imitation gold wares sometimes consist of alloys of copper with aluminium, zinc, &c., and sometimes of a thin plate of gold soldered to a bar of base metal and rolled out for use in manufacture. Electro-plating is carried out in baths containing potassium aurocyanide with anodes of pure gold. The bath is used hot and the anode is of about the same dimensions as the article to be gilded. Gold chloride is added to the bath as required to keep it at the strength of about one ounce of gold to the gallon (6·85 g. of gold per litre). In Japanese art, alloys of copper containing a small proportion of gold are used to enable a beautiful purple patina to be produced on the surface.

Gold leaf contains from 90 to 98 p.c. of gold, the rest being silver and copper. The metal is cast into little flat bars which are rolled out with frequent annealings until about 0·33 mm. thick. The strip of gold is then cut into pieces of 1 inch square and these are interleaved with vellum and beaten with a 16-lb. hammer to 4 inches square. They are again cut up and beaten out between gold-beaters' skins. The book of 25 leaves, each about 3¼ inches (8·25 cm.) square, contains from 4 to 10 grains (0·26 to 0·65 gram) of gold. The leaves are from 0·00008 to 0·0002 mm. thick.

Production of gold.—The annual production of gold, after remaining nearly stationary at 5,000,000 or 6,000,000 ozs. for many years, began to rise rapidly in 1891 and amounted to 22,200,000 ozs. of the value of 94,300,000*l.* in 1909, and about 23,000,000 ozs. of the value of 97,750,000*l.* in 1910. It is still increasing, owing to improvements in the methods of extraction, which enable ore of lower grade than formerly to be treated at a profit. Many countries contribute to the output, and of these the Transvaal, United States, Australia, Russia, Mexico, Rhodesia, India, and Canada between them are responsible for 90 p.c. of the world's production. The British Empire produces about 59 p.c. of the total amount. The world's stock of gold is estimated at 1,400,000,000*l.*, of which the British Empire holds about 250,000,000*l.*

Bibliography.—A full bibliography of gold is appended to the Metallurgy of Gold, by T. K.

Rose, 5th edit., London, 1906. The following are among the most important treatises on the metallurgy of gold published of late years: The Stamp Milling of Gold Ores, by T. A. Rickard, New York and London, 3rd ed., 1901; Ore Dressing, by R. H. Richards, New York, 1903; Cyaniding Gold and Silver Ores, by H. F. Julian and E. Smart, London, 1904; Gold Dredging, by C. C. Longridge, London, 1905.

T. K. R.

Compounds of Gold.

Two oxides are known, the monoxide or suboxide Au_2O, and the sesquioxide or peroxide Au_2O_3 (Bullnheimer, Chem. Zentr. 1897, i. 522; Vanino, Ber. 1905, 38, 462). Auroauric oxide $(AuO)n$ is formed by the partial decomposition of auric hydroxide at 160°.

The *hydroxide* $Au(OH)_3$ is best prepared by heating a solution of gold chloride with magnesia, and washing the residue with nitric acid. It may be obtained pure by reducing potassium auribromide, $KAuBr_4$, with sulphurous acid, and then warming with dilute potassium hydroxide.

It possesses a yellow, olive-green, or brown colour (according to the method of preparation) while damp, and becomes brownish or black on drying. When warmed with alcoholic potash, metallic gold is precipitated in minute scales, used in *miniature painting*.

The hydroxide is soluble in potash, with formation of a very unstable *potassium aurate*. The solution may be used in electrogilding.

The alkali earth aurates have also been obtained. They are stable when dry, but decompose readily in solution under the influence of heat or light. With organic matter they yield explosive powders (Meyer, *l.c.*). When a sheet of gold is used as a positive electrode in sulphuric or nitric acid, a reddish brown explosive powder, probably a hydroxide of gold, is formed (Hampe, Chem. Zeit. 14, 1778).

When acted upon by ammonia, the oxide produces a green or brown *fulminate* allied to that of silver. The fulminate may be obtained as a buff-coloured precipitate, containing some ammoniacal subchloride of gold, on addition of ammonia to gold chloride solution.

Aurous sulphide Au_2S is formed when sulphuretted hydrogen is passed into an acidified solution of gold cyanide or chloride. It is a brown powder, soluble in water when moist, and forms double salts with potassium and sodium sulphites (Ditte, Compt. rend. 1895, 120, 320; Antony and Lucchesi, Gazz. chim. ital. 1896, 26, ii. 350).

Auroauric sulphide Au_2S_2 is formed by passing sulphuretted hydrogen into a cold neutral solution of gold chloride (Antony and Lucchesi, Gazz. chim. ital. 1889, 19, 545; 1891, 21, ii. 209; Christy, J. Soc. Chem. Ind. 1897, 332).

Auric sulphide Au_2S_3 is obtained as a deep yellow precipitate, by treating anhydrous lithium aurichloride with sulphuretted hydrogen at −10° (Antony and Lucchesi, Gazz. chim. ital. 1890, 20, 601, and *l.c.*). It is a graphitic amorphous powder, sp.gr. 8·754 and decomposes at 197°–200° into its elements. Caustic alkalis and hydro- and poly- sulphides of ammonia decompose it with deposition of metallic gold. The three sulphides form colloidal solutions in alcohol.

When finely divided gold is heated with sulphur and potassium carbonate, a double sulphide of potassium and gold, which resists a red heat and is soluble in water, is obtained. It is employed for the production of *Burgos lustre* in gilding china.

Various gold sodium, potassium, and ammonium sulphites and thiosulphites have been obtained (Antony and Lucchesi, *l.c.*). The sulphites, $K_5[Au(SO_3)_4],5H_2O$; $Na_5[Au(SO_3)_4],14H_2O$; $Au_2(SO_3)_2,4NH_3,4H_2O$; and

$$Au(SO_3)_2K_3,2NH_3,2H_2O$$

are described by Pritze (Zeitsch. anorg. Chem. 1908, 59, 198), whilst the compound $AuS_2{\cdot}NH_2$ has been prepared by Hofmann and Höchtlen (Ber. 1903, 36, 3090; 1904, 37, 245).

Thiosulphate of gold and sodium

$$Au_2S_2O_3{\cdot}3Na_2S_2O_3,4H_2O$$

crystallises in colourless needles, freely soluble in water. It is formed by the action of sodium thiosulphate on gold chloride. This salt exists in combined fixing and toning photographic baths.

Aurous chloride AuCl is formed by heating the trichloride at 170°–180°. It is a yellowish powder, sp.gr. 7·4, which combines with chlorine at ordinary temperature forming auric chloride and decomposes into its elements at about 185° (Rose, Chem. Soc. Trans. 1895, 881, 905; Campbell, Trans. Faraday Soc. 1907, 3, 103). It is insoluble in water, but decomposed by it with the formation of auric chloride and metallic gold. It dissolves in a solution of potassium bromide forming metallic gold and potassium aurichloride and bromide (Lengfeld, Amer. Chem. J. 1901, 26, 324). Liquid ammonia reacts on aurous chloride forming $AuCl,12NH_3$ which loses ammonia on warming and yields $AuCl,3NH_3$ which when heated to 180° is decomposed with formation of ammonium chloride and gold (Meyer, Compt. rend. 1906, 143, 280).

Auric chloride or **trichloride** $AuCl_3$ is prepared by dissolving gold in *aqua regia* and evaporating the solution to dryness at a temperature below 120°, the hydrochloric acid being always kept in excess over the nitric acid. The residue is dissolved in water and filtered from the aurous chloride which is always produced, and the solution is evaporated on the water-bath. Large orange-coloured efflorescent crystals of the hydrated chloride $AuCl_3,2H_2O$ are thus produced.

According to Thomsen, the chloride is best prepared as follows. Powdered gold is converted by the action of chlorine into the dark-red crystalline dichloride, and a little water is added to convert it into a mixture of mono- and trichlorides. The mass is heated gently to decompose the former, and the residue is dissolved in water, filtered from the reduced metal, evaporated and heated to 150°, with production of a brown crystalline mass of the anhydrous chloride. The chloride is also formed when gold is treated with fuming hydrochloric acid in the presence of a trace of manganous chloride and the mixture is exposed to light (Berthelot, Compt. rend. 1904, 138, 1297).

If gold is treated with liquid chlorine in a sealed tube at the ordinary temperature, the metal is converted into a crystalline red mass, but when heated at 100°, the gold dissolves

entirely, forming a deep yellow solution from which, on cooling, auric chloride separates in wine-red hygroscopic crystals.

Between 170° and 240° auric chloride dissociates into aurous chloride and chlorine (Meyer, Compt. rend. 1901, 133, 815; Rose, *l.c.*).

Under the influence of heat or light, auric chloride is decomposed in solution, thus:

$$AuCl_3+2H_2O=AuCl+2HCl+H_2O_2$$

and $3AuCl=2Au+AuCl_3$ (Sonstadt, Chem. News, 1898, 77, 74; Chem. Soc. Proc. 1898, 179; Löwe, Dingl. poly. J. 279, 167). Manganous and uranous sulphate and also manganous chloride reduce gold chloride in the dark, precipitating metallic gold. The process is accelerated in the former case by heat, in the two latter by sunlight (Oechsner de Coninck, Bull. Acad. Roy. Belg, 1902, 316).

Gold chloride is also reduced by charcoal thus:

$$4AuCl_3+6H_2O+3C=4Au+12HCl+3CO_2$$

(Avory, J. Soc. Chem. Ind. 1908, 255; Hay and Tennent, Amer. Chem. J. 1909, 31, 461); by acetylene (Mathews and Watters, J. Amer. Chem. Soc. 1900, 22, 108); and by sulphuretted hydrogen under certain conditions (Schneider, Ber. 1891, 24, 2241; Antony and Lucchesi, Gazz. chim. ital. 1889, 19, 545).

When heated to 200°, the trichloride is resolved into a mixture of aurous chloride and gold. At a higher temperature the whole of the chlorine is given off.

Auric chloride is freely soluble in water, alcohol, and ether. It forms a crystalline compound, $AuCl_3,HCl,4H_2O$, with hydrochloric acid, and forms double chlorides with the alkali metals and with organic bases (Lainer, Monatsh. 11, 220).

Auric chloride and the sodium and potassium salts, such as $NaCl,AuCl_3,2H_2O$, are employed for toning silver prints in photography (Kebler, J. Franklin Inst. 1900, 150, 235; Johnson, J. Soc. Chem. Ind. 1901, 210). Other alkali double chlorides are described by Wells and Wheeler (Amer. J. Sci. [3] 44, 157).

Gold chloride forms salts with pyridine, such as $C_5H_5N,AuCl_3$, $(C_5H_5N)_2AuCl_3$ (François, Compt. rend. 1903, 136, 1557). Aurophosphorous chloride $(AuPCl_2)Cl$ and complex organic compounds of phosphorus and gold chloride are described by Levi Malvano (Atti R. Accad. Lincei, 1908, [v.] 17, i. 847). The acetates and succinates are used in photography (Mercier, Brit. Journ. Phot. 39, 354).

Chloroauric acid $AuCl_3,HCl$, prepared by the action of chlorine on gold suspended in hydrochloric acid (Lengfeld, Amer. Chem. J. 1901, 26, 324), reacts with silver nitrate, forming a brown precipitate, $Au(OH)_3,4AgCl$, which, with ammonia, forms gold fulminate, $Au(OH)_3NH_3$ or $Au_2O_3,2H_2O,H_2O$. Gold fulminate is very explosive when dry, and when heated with potash forms a [illegible] brownish-black product, probably $Au(HO)_2{\cdot}NH{\cdot}Au(OH)_3$, which is still more explosive (Jacobson, Compt. rend. 1908, [illegible]). Chloroauric acid forms salts such as $KAuCl_4$, &c. (Lengfeld, *l.c.*).

By the action of aurochloric acid on sodium [illegible] an orange crystalline very explosive compound is obtained (Curtius and Rissom, [illegible]. Chem. [illegible], [ii.] 58, 261).

Aurous bromide AuBr is a greenish yellow powder, which is formed by heating auribromic acid at 115°. Its properties are very similar to those of the corresponding chloride (Meyer, *l.c.*).

Auric bromide $AuBr_3$ is formed by the action of dry bromine on powdered gold; when heated it dissociates forming the monobromide (Meyer, Compt. rend. 1909, 148, 346). According to Lengfeld (*l.c.*), aurous bromoaurate Au_2Br_4 also exists. Bromoauric acid and bromoaurates have also been prepared.

Aurous iodide can be prepared by the action of excess of pure iodine on metallic gold above 50°, the excess of iodine being then removed by careful sublimation (Meyer, Compt. rend. 1904, 139, 733). It is also formed by the action of hydriodic acid on gold oxide. It is a white powder, turning green in air and decomposing at 190°; it is also decomposed by solvents such as chloroform. With liquid or gaseous ammonia, it forms $AuI,6NH_3$ and AuI,NH_3 (Meyer, *ibid.* 1906, 143, 280). Auric iodide probably does not exist.

Gold fluoride has been described by Lenher (J. Amer. Chem. Soc. 1903, 25, 1136).

Gold chromate can be obtained by treating silver chromate with auric chloride; $Au_2(CrO_4)_3$ is obtained in solution, whilst the chromate $Au_2(CrO_4)_3CrO_3$ crystallises from the mother liquor (Orloff, Chem. Zeit. 1907, 31, 1182).

When solutions of sodium aurate and chromate are mixed, sodium aurochromate containing excess of chromate is obtained, the solution of which forms an excellent toning bath, giving purple bluish tones. It is neutral and can be kept, and the yellow colour allows the toning to be done in daylight (Mercier, Chem. Zeit. Rep. 24, 272; J. Soc. Chem. Ind. 1900, 1038).

Gold carbide Au_2C_2 is formed by passing acetylene into aurous thiosulphate. It is very explosive when dry and is decomposed by hydrochloric acid, forming acetylene and aurous chloride. Treated with water it yields gold and carbon (Mathews and Watters, *l.c.*).

The following gold salts have also been obtained: arsenates (Stavenhagen, J. pr. Chem. 1895 [2] 51, 1); selenates and tellurates (Lenher, J. Amer. Chem. Soc. 1902, 24, 354, 355, 918); various alkyl gold chlorides (Pope and Gibson, Chem. Soc. Trans. 1907, 2061); thiocarbamides (Moir, *ibid.* 1906, 1345); mercaptides (Herrmann, Ber. 1905, 38, 2813), and other complex organic compounds (Dunstan and Shepheard, Chem. Soc. Proc. 1893, 212; Weigand, Zeitsch. angew. Chem. 1906, 19, 139; Averkieff, J. Russ. Phys. Chem. Soc. 1908, 40, 840).

The thio-compounds of certain resins and ethereal or fatty oils or thioacids, yield compounds with gold which are soluble in most organic solvents and which can be employed in the ceramic enamel and glass industries for the deposition of the finest layers of bright metal on various substances (Pertsch, Frdl. 1894-97, 1324).

According to Odenheimer (J. Soc. Chem. Ind. 1892, 600), textile fabrics padded or printed with a gold salt and then treated with a reducing agent assume a beautiful grey colour, the process being accelerated by heat or sunlight. The shade depends on the nature of the reducing agents employed and on the strength of the gold solution. When these grey fabrics are subjected to heat between rollers, red, purple, or pink colours

are obtained, depending on the original shade of grey. The high price of gold is no disadvantage in this process as only a very minute quantity of gold solution is required. Thus, for a beautiful pearl grey on half silk, the cost is only ¼*d.* per lb. of material dyed.

Gold cyanides (*see* ELECTROPLATING and CYANIDES).

GOLD, MANNHEIM. A brass containing 80 p.c. of copper and 20 p.c. of zinc.

GOLD, MOSAIC. A fine, flaky yellow form of tin disulphide; is used in the arts to imitate bronze under this title, and is preferably prepared as follows. A mixture of 7 parts of sulphur, 6 parts of ammonium chloride, and 18 parts of a powdered amalgam containing 2 parts of tin to 1 part of mercury, is heated gently until the smell of sulphuretted hydrogen is no longer perceptible. The heat is then raised to low redness, and a mixture of mercurous chloride, ammonium chloride, and cinnabar sublimes, while the mosaic gold alone remains. A fine product is also obtained by heating a mixture of 5 parts of stannous sulphide and 8 parts of mercuric chloride.

The essential point is that tin must be present in a volatile form; stannous chloride itself may be used.

A pale-yellow mosaic gold is produced by heating 50 parts crystalline stannous chloride with 25 parts flowers of sulphur; a reddish-yellow product is obtained on heating together 50 parts 50 p.c. tin-amalgam, 25 parts stannous chloride, 35 parts ammonium chloride and 35 parts of sulphur. 57 p.c. of the tin taken is obtained as the sulphide (Lagutt, Zeitsch. angew. Chem. 1897, 557).

The temperature should not be too high, as the stannic sulphide, when strongly heated, loses one equivalent of sulphur and becomes black.

Mosaic gold is insoluble in nitric and hydrochloric acids, but dissolves in *aqua regia* and in alkaline hydroxides.

A brass, introduced by Hamilton and Parker (Edinb. J. of Sc. 1826), and containing 52 to 55 p.c. of zinc, is also known by this name. A mixture of equal parts of zinc and copper is fused at the lowest possible temperature, and zinc is slowly added, with constant stirring, until the desired colour is produced. The colour passes from a brassy yellow to a purple or violet, and finally becomes perfectly white. The mass, when cooled, has the colour of gold, and is said to be not liable to tarnish.

GOLD, ORANGE, *v.* AZO-COLOURING MATTERS.

GOLD PURPLE (*Purple of Cassius*). This compound is obtained as a fine, flocculent purple precipitate on addition of a solution of stannous chloride containing stannic chloride, to a dilute neutral solution of gold chloride. The presence of the stannic chloride is essential, as pure stannous chloride produces only a brown precipitate.

A very fine product is obtained by adding stannous chloride to ferric chloride until the solution is of a pale-green colour, and employing the mixture to precipitate the gold solution. According to another process, 1 part of tin is dissolved in the minimum of hydrochloric acid, and 2 parts of the tin are dissolved in a cold mixture of 3 parts of nitric acid and 1 part of hydrochloric acid, the solution being finally heated to ensure conversion of all the tin into stannic chloride. A solution of 7 parts of gold in a mixture of 6 parts of hydrochloric acid and 1 part of nitric acid is diluted with 3,500 parts of water, and the solution of the stannic chloride is added, the stannous chloride being then added in drops until the required colour (from violet to purple or brown) is obtained (Baisson).

According to Pelletier, a purple of Cassius of constant composition is obtained as follows. A solution of as much gold chloride as contains 20 grains of gold is diluted to 700 or 800 c.c., and tin filings are introduced. The liquid speedily becomes brown and turbid, and finally deposits the purple, which is washed and dried. It is said to contain 32·75 p.c. of stannic oxide. 14·62 p.c. of stannous oxide, 44·77 p.c. of aurous oxide, and 7·86 p.c. of water.

Purple of Cassius may also be obtained in great beauty by treating an alloy of gold 2 parts, tin 3·5 parts, and silver 15 parts, with nitric acid to remove the silver and oxidise the tin.

Zsigmondy (Annalen, 301, 361) prepares purple of Cassius by mixing 200 c.c. of gold chloride (3 grams Au per litre) with 250 c.c. stannous chloride (3 grams Sn per litre) and 4 litres of water. After 3 days, the purple is deposited, leaving a liquid free from gold and tin. The precipitate thus prepared contains, after ignition, 40·3 p.c. gold and 59·7 p.c. stannic oxides.

According to Moissan (Compt. rend. 1905, 141, 977), when gold-tin alloys are distilled in air, a finely divided mixture of stannic oxide, lime, and gold is obtained, having the colour and properties of purple of Cassius. Similar deposits of varying tint can be obtained by substituting for lime other oxides such as zirconia, silica, magnesia, or alumina.

Schneider (Zeitsch. anorg. Chem. 1893, 5, 80) obtained an aqueous solution of gold purple by treating an alloy of gold, tin, and silver with concentrated nitric acid. When the resulting black powder is washed with ammonia, a ruby-red coloured solution is obtained, which is dialysed until it contains no more ammonia. It contains 0·5800 gram of gold and 5·4048 grams of stannic oxide per litre.

Potassium cyanide decolourises the solution and stannic acid separates. With mercury, the solution becomes brownish red and gold is extracted; whilst with excess of hydrochloric acid, the solution becomes violet and yields finely divided gold on dialysis. According to this author, the soluble form of purple gold is, possibly, a mixture of the hydrosols of gold and stannic acid.

This body, which is used in the manufacture of artificial gems (*v.* GEMS, IMITATION AND COUNTERFEIT), and for imparting a red, rose, or pink colour to porcelain or enamel, varies in colour from a violet to a purplish red or brown. The dry precipitate is insoluble in strong or dilute alkalis, but when moist the purple dissolves in water in the presence of very small quantities of acids and alkalis. Salts and excess of alkalis and acids precipitate the purple from these solutions.

While moist, it is also soluble in ammonia with production of a purple colour, from which the precipitate is redeposited on addition of an acid or on boiling, and, in the latter case, is not

again soluble. The ammoniacal solution precipitates gold on exposure to light. The purple does not pass through the membrane of a dialyser.

When dried and triturated, the purple of Cassius acquires a metallic lustre. No gold is removed from it by the action of mercury. It retains water at 100°, but gives it up and acquires a brick-red colour when ignited, and loses its colour at the melting-point of gold, but without evolution of oxygen.

On adding a greater quantity of mercurous chloride to a solution of auric chloride than that required for the reaction

$$3HgCl+AuCl_3=3HgCl_2+Au,$$

the characteristic colour of purple of Cassius is obtained. If barium sulphate suspended in water is previously mixed with the mercurous chloride, the sulphate takes up the gold and becomes the colour of the purple. Antony and Lucchesi (Gazz. chim. ital. 1896, ii. 195) therefore regard true purple of Cassius as being, not a compound, but merely stannic acid mechanically covered with gold.

The constitution of this substance, of which the composition, as found by analysis, is very variable, is not yet established. Berzelius, judging from the researches of Figuier, considered it to be a hydrated stannate of gold and tin. Macquer looked upon it as a mixture of stannic hydroxide and metallic gold; and Proust considered it to be a mixture of aurostannous stannate and stannic hydroxide.

Zsigmondy regards the purple as a mixture of colloidal gold and colloidal stannic acid; the gold acquiring the property of dissolving in very dilute acids through the presence of the stannic acid which is soluble in them. A mixture of colloids may thus behave as a chemical individual where the properties of one of the constituents may be completely hidden.

Debray (Compt. rend. 75, 1025), and also Moissan (*l.c.*), look upon it as allied to the *lakes*, and as consisting of gold combined with stannic acid, in the same way as the colouring matter of the lake is combined with alumina, the gold being insoluble in mercury, as the colouring matter is insoluble in water. Debray has prepared the purple by boiling freshly precipitated stannic hydroxide with a mixture of gold chloride and potassium oxalate. The action of ammonia on the purple is similar to its action on stannic hydroxide, both being soluble while moist, but becoming insoluble when anhydrous.

The fact that the ammoniacal solution precipitates gold is in favour of the view that the gold is present in the metallic state, as ammonia is not known to precipitate precious metals by action on their oxides.

Debray has also produced a purple by replacing the stannic hydroxide by alumina.

Müller (J. pr. Chem. [ii.] 30, 252) has prepared purples by several processes without the use of tin. A pale rose (containing 0·1 p.c. of gold) to deep carmine pigment is produced by igniting a well washed and dried mixture of magnesium oxide and gold chloride. A similar result is obtained by heating the mixture in a current of hydrogen.

Lime, calcium carbonate, calcium phosphate, barium sulphate, and lead and zinc oxides give similar but less satisfactory results.

The most intense purple is, however, obtained by reducing a mixture of aluminium hydroxide and gold chloride with alkaline grape-sugar solution. The mixture is agitated and heated until of a bright scarlet colour, but the colour must not be allowed to reach a purplish red, or the resultant product will be of inferior brilliancy.

Similar but less brilliant purples than those with magnesia and alumina are obtained with tin. As much stannous chloride as corresponds with 9 grams of stannic oxide, is dissolved in 200 c.c. of water, and the solution is rendered alkaline by addition of potassium carbonate. Grape sugar solution is added, and the mixture is diluted to 300 litres, and is warmed until of the best colour.

These methods of preparation uphold the view that the gold is present in the metallic state.

Red, blue, violet, and green colloidal solutions of gold can be readily prepared. Colloidal solutions of gold can be formed by the addition of gold chloride solution to water, containing small quantities of the following substances: turpentine oil, pinene, rosemary oil, or potassium carbonate with formaldehyde, pinene, turpentine oil, or alcohol. The formation of the colloidal solution can be accelerated by adding to the gold chloride solution a few drops of gold solution already in the colloidal state. The colour of the solutions depends on the temperature and the concentration (Vanino and Hartl, Ber. 1905, 38, 463; 1906, 39, 1696; Zsigmondy, Zeitsch. physikal. Chem. 1906, 56, 65; Henrich, Ber. 1903, 36, 609; Garbowski, *ibid.* 1215). Colloidal gold can also be precipitated by the action of formaldehyde on gold chloride in the presence of sodium hydroxide (Zsigmondy, Annalen, 1898, 301, 29; Zeitsch. Chem. Ind. Kolloide, 1907, i. 272).

Carey Lea (Zeitsch. anorg. Chem. 1897, 13, 447) obtained a beautiful green solution by mixing a 10 p.c. sodium hyposulphite solution with 1 c.c. of gold chloride solution (10 c.c. = 1 gram gold) and a drop of sulphuric acid. As soon as the solution begins to darken, 30 c.c. of water are added. Gradually, a bluish black precipitate of metallic gold separates; after filtration, the green solution again becomes turbid. If the solution is shaken and allowed to remain, a precipitate of gold is deposited on the sides of the vessel, which is yellowish brown by reflected light and bright blue by transmitted light.

Humic acid, added to gold chloride, produces colloidal gold solutions of various colours, depending on the conditions of the experiment (Ehrenberg and Pick, Zeitsch. chem. Ind. Kolloide, 1909, 5, 30).

When 1 litre of water containing 1 gram of auric chloride and made just alkaline with sodium carbonate, is boiled, and then poured into 300 c.c. of a cold solution of catechol (pyrocatechin) containing 11 grams per litre, a red colouration is produced, rapidly turning to violet. On mixing 10 such preparations and just acidifying with sulphuric acid, the liquid becomes blue and deposits a blue powder which is washed with water, then with alcohol, is dissolved in ammonia and can be reprecipitated by sulphuric acid. The substance manifests acid properties, forming salts with some of the heavy

metals (Henriot, Compt. rend. 1904, 138, 1044).

A stable solution of colloidal gold of therapeutic value is obtained by reducing with atoxyl (*p*-aminophenylarsinate) a gold chloride solution made faintly alkaline with sodium hydrogen carbonate. Similar solutions are also obtained by reduction with sodium sulphanilate or naphthionate. When evaporated to dryness in a vacuum, a grey residue is obtained which dissolves completely in water, forming a characteristic ruby red solution of colloidal gold (Poulenc Frères, D. R. P. 206343).

Red to purple colloidal solutions may be obtained by passing carbon monoxide, pure, or mixed with carbon dioxide, through a solution of auric chloride in conductivity water, containing 0·002–0·05 p.c. gold (Donau, Monatsh. 1905, 26, 525). Similar solutions have also been obtained by reducing very dilute solutions of gold chloride with phenylhydrazine hydrochloride (Gutbier and Resenschek, Zeitsch. anorg. Chem. 1904, 39, 112), hydrazine hydrate (Gutbier, *ibid.* 1902, 31, 448), hydroxylamine hydrochloride (*ibid.* 1902, 32, 347), or with sodium lysalbate or protalbate (Paal, Ber. 1902, 35, 2236): also by the action of *Aspergillus oryzæ* on 0·01 gram gold chloride in 100 c.c. water (Vanino and Hartl, *ibid.* 1904, 37, 3620). An electric discharge between gold poles also gives reddish purple or dark blue solutions, which can be filtered without change and retain their colour for months (Bredig, Zeitsch. angew. Chem. 1898, 951; Bredig and Reinders, Zeitsch. physikal. Chem. 1901, 37, 323). Various other methods of preparing colloidal gold solutions and precipitates have been proposed (Schottländer, Chem. Zentr. 1894, ii. 409; Brunck, Annalen, 1903, 327, 240; Donau, Monatsh. 1904, 25, 545; Whitney and Blake, J. Amer. Chem. Soc. 1904, 26, 1339; Vanino and Hartl, Chem. Zentr. 1907, i. 1099; Vanino, *ibid.* 1908, i. 446; Dauvé, J. Pharm. Chim. 1909, 29, 241; Doerinckel, Zeitsch. anorg. Chem. 1909, 63, 344).

Gold chloride solution, with water glass and formalin heated on the water-bath gives, according to quantity, bright red, claret-red, blue, or even green colloidal solutions. Very small amounts of gold gave a rose red colouration (Kuspert, Ber. 1902, 35, 4070).

According to Stenberg (Ann. Physik. 1908, [iv.] 26, 329), the various colours of colloidal gold solutions are due to the difference in form of the particles. Distinct forms of particles exist for the red and blue solutions; the violet colour is produced by a mixture of these, whilst green solutions are due to the condensation of the particles which give rise to the red and blue colour.

The liquid hydrosols of gold are decolourised when shaken with animal charcoal, barium sulphate, powdered porcelain, amorphous silica, fibres of filter paper or with electrolytes, but if gum arabic or gelatin is present, this reaction is prevented or diminished (Donau, Monatsh. 1905, 26, 525). An electric current in the presence of various electrolytes changes the red colloidal solutions into blue (Blake, Amer. J. Sci. 1903, [iv.] 16, 433).

Silk and cotton fibres treated with tannin or stannous chloride and pyrogallol, are coloured red and blue respectively, on addition of gold chloride. This colour is destroyed by concentrated acids, free halogens, and reducing agents, but not by dilute acids or alkalis.

GOLD, YELLOW, *v.* VICTORIA YELLOW.

GOLDEN YELLOW *v.* NAPHTHALENE.

GOMART RESIN *v.* OLEO-RESINS.

GOOSEBERRY. The fruit of *Ribes grossularia* (Linn.). There are many varieties, differing in shape, size, texture, and colour.

They are largely used both immature and ripe, in cookery, as raw fruit and in jam making. The average composition, deduced from 34 analyses, is given by König as follows:—

Water	Protein	Free acid	Invert sugar	Saccharose	Other carbohydrates	Fibre	Ash
83·6	0·5	1·4	7·1	0·9	0·6	3·5	0·4

The acidity is chiefly due to malic acid.

H. I.

GORNEROL. Trade name for an essential oil prepared from the leaves of *Melaleuca leucadendron* (Linn.) (Nat. Ord. *Myrtaceæ*) of New Caledonia, similar to, if not identical with, oil of Cajuput (*q.v.* under art. OILS, ESSENTIAL). Known also as Niaoul oil.

GORSE, called also **FURZE** and **WHIN.** *Ulex europæus* (Linn.). A plant belonging to the *leguminosæ*, and therefore capable, by the aid of symbiotic bacteria, of fixing atmospheric nitrogen.

It will grow in soils poor in mineral matter, and has been strongly recommended as a fodder plant, for littering, and as a green manure. It is estimated that a crop of 20,000 kilos. per hectare may be obtained, and that this, in feeding value, is equal to 8000 kilos. of hay.

Average composition, according to Girard (Ann. Agron. 1901, 27, 5):

Water	Protein	Fat	N-free extract	Cellulose	Ash
52·7	4·6	0·9	26·0	14·5	1·6

The N-free extract includes about 1·4 p.c. sugar, 9 p.c. pentosans, and 1·6 p.c. pectin.

The ash contains:

K_2O	CaO	MgO	Fe_2O_3	P_2O_5	SO_3
27·1	11·7	4·3	2·4	6·7	4·7

With horses the digestion coefficients obtained were as follows: Ash 40, fat 22, protein 56, cellulose 43, sugar 100, total non-nitrogenous matter 55. With sheep the figures were lower. Only the tender young shoots are readily eaten by animals, unless the material be well crushed, so as to soften and break the prickles.

Experiments in 1899 and 1901 by Voelcker (Jour. Roy. Agric. Soc. for these years) showed that with sheep, gorse, properly comminuted by special machinery, could, with advantage, replace a portion of the roots used in feeding. Not more than 9 or 10 lbs. of gorse per head per week, however, could be used.

J. I.

GOSSYPITRIN *v.* GLUCOSIDES.

GOUDANG WAX *v.* WAXES.

END OF THE SECOND VOLUME.

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